STUDIES OF ARTIFICIAL CARBON-14 IN THE CARBON CYCLE

THESIS
submitted for the degree of
DOCTOR OF PHILOSOPHY
of the
UNIVERSITY OF GLASGOW
by
MEHMET ERGIN

December, 1969.

ProQuest LLC.
789 East Eisenhower Parkway
P.O. Box 1346
Ann Arbor, MI 48106 – 1346

SUMMARY

The basic assumption of the radiocarbon dating method is that the carbon-14 concentrations in the atmosphere have remained essentially constant in the past although there is some evidence that fluctuations have occurred during the past 10 millennia. These fluctuations are reflected in biospheric and oceanic carbon-14 concentrations since the distribution of carbon-14 is controlled by the exchange processes between the respective reservoirs. A precise knowledge of these exchange rates is desirable, therefore, if past carbon-14 fluctuations are to be explained and future carbon-14 concentrations predicted. Evaluation of these parameters also yields important data for the study and understanding of meteorological, biological and oceanographic processes.

Some estimates of exchange rates have been made on the basis of measured carbon-14 variations during the past 20 years as a result of the Suess effect. Further studies have been based on the artificial carbon-14 produced prior to the major test series of 1961-62.

During 1961-62 large-scale atmospheric testing of thermonuclear devices produced substantial quantities of carbon-14 through the interaction of escaping neutrons from the weapons with atmospheric nitrogen, $^{14}N(n,^{1}H)\,^{14}C$. Prior to 1961 the amount of carbon-14 produced by nuclear weapons amounted to

only about one third that produced in the new test series. Thus the most recent amounts produced can be regarded as a new tracer for the study of the distribution and exchange rates of carbon dioxide between the various dynamic carbon reservoirs, i.e., the troposphere, stratosphere, ocean surface layer, deep ocean and biosphere.

During 1967 and 1968 extensive measurements were made of the carbon-14 concentrations in tropospheric carbon dioxide samples collected at a world-wide network of sampling stations. These results, together with the stratospheric and oceanic data have been used to calculate the inventories of artificial carbon-14 in various reservoirs of the carbon cycle for July 1967 and 1968.

Residence times of carbon dioxide in various reservoirs of the carbon cycle have also been studied using a number of "chain" and "cyclic" models of varying complexity. The calculated exchange rate parameters indicate that both the ocean and biosphere are important in determining the atmospheric carbon-14 level. The magnitude of the exchange processes between the atmosphere and each of these reservoirs are comparable. However, the relatively large size of the oceanic reservoir suggests that this is the major controlling factor over the long term.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

CHAPTER 1. INTRODUCTION

Since the beginning of nuclear testing many studies have been made of atmospheric mixing processes using particulate fission products as tracers. The data obtained from these studies cannot be expected to yield true results for the mixing rates of air masses since the solid particles are washed out of the atmosphere by rain within a relatively short period of time ranging from six to eight weeks. Gaseous substances, on the other hand, such as CO_2, remain in the atmosphere for longer periods and their residence times are controlled by the rates of exchange between the atmosphere, ocean and biosphere.

During 1961 and 1962 large-scale nuclear testing produced unprecedented amounts of artificial carbon-14 through the interaction of escaping neutrons with atmospheric nitrogen, $^{14}N \xrightarrow{np} {}^{14}C$. This artificial activity was added mainly to the stratosphere where it was presumably oxidized to CO_2 quite rapidly. An ideal opportunity was therefore created for a "tracer" study of atmospheric mixing and transfer processes. In fact, as a result of these mixing processes the carbon-14 has now become distributed throughout the stratosphere and troposphere. The actual increase in the tropospheric carbon-14 concentration of the northern hemisphere reached 100% above the natural level in mid 1963. Further exchange between the troposphere and the oceans has resulted in an increase in the carbon-14 concentration in the surface ocean water which is now easily detectable. With these distribution

patterns of carbon-14 it is now possible to evaluate the rate of CO_2 exchange between the atmosphere and the oceans with much better accuracy than has been possible in the past.

Since the specific activity of carbon-14 in the atmosphere is influenced by these exchange mechanisms, and since the radiocarbon dating method assumes a constancy of carbon-14 concentrations in the atmosphere, it is obviously important, therefore, to gain a full understanding of these processes. In fact, recent studies on tree rings have shown that the specific activity of carbon-14 in the atmosphere has probably fluctuated considerably in the past. The reasons for these fluctuations can be either a change in the natural production rate of carbon-14 by cosmic rays, or variations in the mixing rates between dynamic carbon reservoirs caused by climatic changes. In either case the amplitude and duration of the fluctuation is primarily controlled by the rate of exchange between the atmosphere and the surface layers of the ocean.

A detailed study of the rate of change of "bomb" carbon-14 concentrations in tropospheric CO_2 will therefore assist in determinations of the parameters controlling exchange patterns and may also yield information of value to considerations of the basic assumptions in the radiocarbon dating method.

1.1. History and Theory of the Radiocarbon Dating Method.

In 1940 Korff suggested the possibility that carbon-14 was continuously being generated in the upper atmosphere by cosmic ray produced neutrons. Later, in 1946 Libby estimated that it

should be possible to detect natural carbon-14 in environmental materials. Libby and his co-workers (Anderson, Weinhouse, Reid, Kirshenbaum and Grosse) (1947) then showed experimentally that naturally produced carbon-14 could be measured and suggested its use as a method of dating.

The important nuclear reactions involving cosmic ray neutrons and the main atmospheric constituents are as follows:

Reaction cross section

a) $^{14}N + n \longrightarrow {}^{14}C + {}^{1}H$ $\sigma = 1.7$ (barns)

b) $^{14}N + n \longrightarrow {}^{11}B + {}^{4}He$ $\sigma \sim 0.2$ at $>$ 1 Mev

c) $^{14}N + n \longrightarrow {}^{12}C + {}^{3}H$ $\sigma \sim 0.01$ at $>$ 4 Mev

d) $^{16}O + n \longrightarrow {}^{17}O + \gamma$

From considerations of the cross sections of these reactions it is clear that reaction (a) is favoured. It follows therefore that the majority of cosmic ray neutrons contribute to the production of carbon-14.

Values for the cosmic ray carbon-14 production rate range from 1.3 to 2.6 atoms/cm^2/sec, Libby (1955), Anderson (1953), Kouts and Yuan (1952), Ladenburg (1952) and Soberman (1956). A re-evaluation of the data by Craig (1957) indicated the best value to be 2.0 ± 0.5 atoms/cm^2/sec. Following their production it is believed that the carbon-14 atoms are rapidly oxidized to $^{14}CO_2$ which then mixes with inert $^{12}CO_2$ and $^{13}CO_2$ in the atmosphere. The carbon-14 thus becomes incorporated in plants through photosynthesis and enters the biosphere. In addition to the contribution of carbon-14 to the biosphere significant quantities are transferred to the hydrosphere via CO_2 exchange.

It was reasoned by Libby (1955) that the average residence time of a radiocarbon atom in any of these reservoirs ("dynamic" carbon cycle) was so short in comparison to its half life, that each atom would complete the cycle of transfer from one reservoir to the other several times throughout its lifetime. It was therefore predicted, and later shown, that the distribution of radiocarbon throughout the dynamic reservoirs was quite uniform. It was also assumed that the cosmic ray intensity had been essentially constant for at least 20,000 to 30,000 years and that the carbon-14 concentration in the dynamic reservoirs had not changed over this time period, Libby (1955). On the basis of these assumptions an equilibrium between the rate of decay and the rate of assimilation of radiocarbon atoms for all living things would be attained while they were alive, but when death occurred, assimilation would cease and only radioactive decay would continue. Hence, the age (t) of a carbon sample can be calculated in the following manner:

$$A_t = A_o \, e^{-\lambda t}$$

where, A_o is the activity of carbon-14 present in the sample on removal from the natural carbon cycle. For an organism this would date the time at which the organism died. A_t is the activity of carbon-14 at time t, and λ is the disintegration constant for carbon-14. If one assumes that when the material to be dated was a part of the carbon cycle it had a carbon-14 specific activity identical to contemporary carbon then A_o may measured in contemporary carbon and the sample's age calculated from the above equation. Libby (1955) substantiated the validity

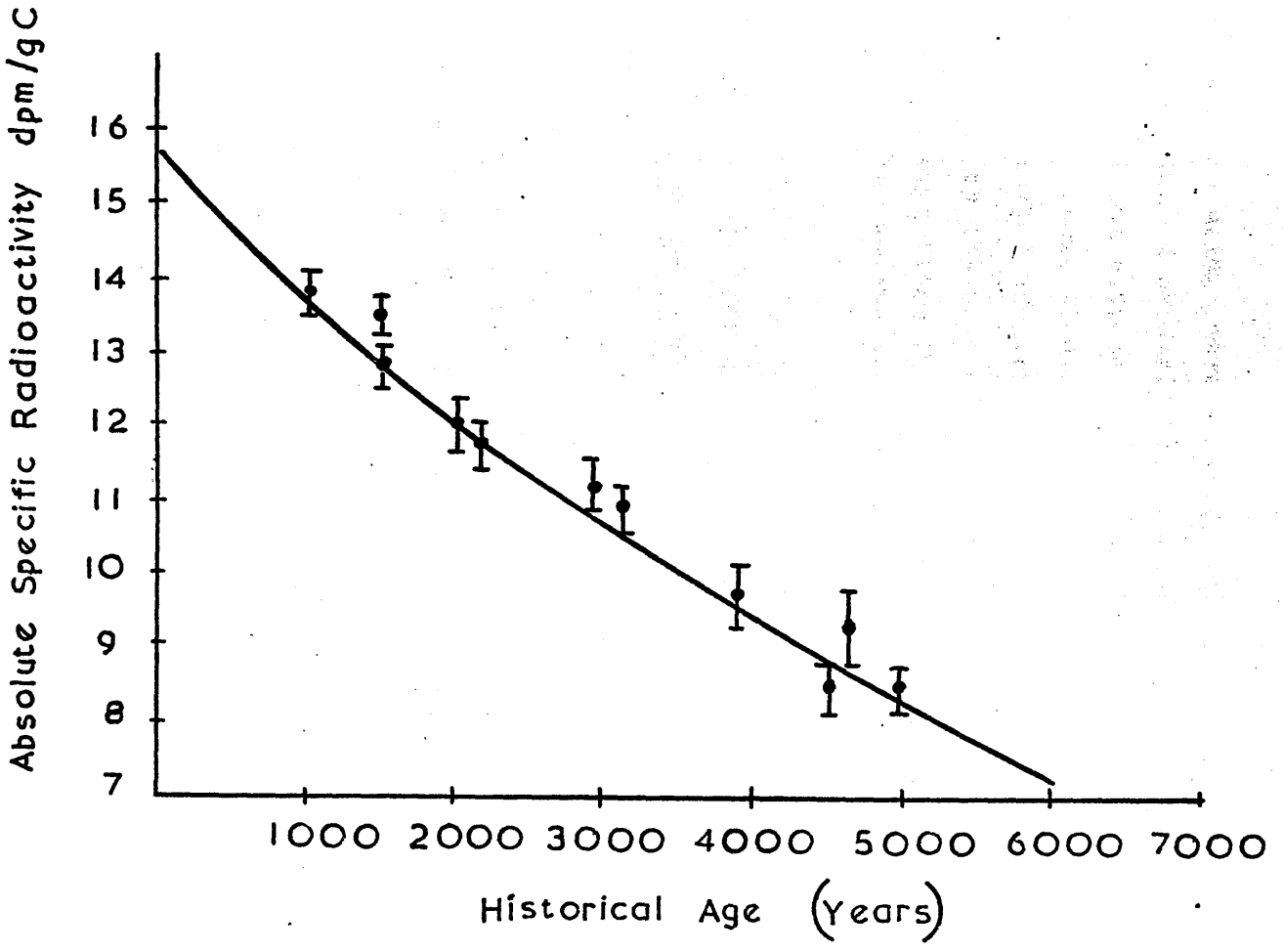
of this method by obtaining excellent agreement between ages determined by the carbon-14 method and ages of historically dated materials (Figure 1.1).

Since its inception the carbon-14 method has become the criterion against which all other methods of chronological determinations of less than 50,000 years have been checked. However, several sources of error have recently been unearthed which have led to a questioning of the validity of some of the basic assumptions. The assumptions currently under examination are (1) that the carbon-14 specific activity in the sample to be dated was originally the same as that of similar material (modern standard) living today; and (2) that the carbon-14 concentration in the sample changes only through radioactive decay after "death." A prerequisite of the first assumption is that the cosmic ray flux must have been relatively constant over the past 50,000 years, and that there has been uniformity of isotopic composition throughout the active carbon reservoir. It has been shown, however, that the specific activity of carbon-14 in the atmosphere has probably fluctuated during the past 10 millennia.

1.2. Fluctuations of Environmental Radiocarbon Concentrations Caused by Natural Effects.

Libby (1955), recognized the possibility that geography may influence radiocarbon concentrations in the environment. To investigate this possibility, samples of different but known ages, collected at various places on the earth, were analysed.

Figure 1.1. Predicted Versus Observed Radioactivities of Samples of Known Age (Libby 1955)



With the facilities available at that time it was impossible to detect any significant variations within the age interval examined.

Later studies, using improved techniques involving gas proportional and liquid scintillation counting, have shown significant deviations between radiocarbon dates and true historical ages. These findings arise from disturbances in the radiocarbon content of living matter which could be caused by (1) variations in the rate of production of radiocarbon by cosmic rays, (2) variations in the size of the reservoirs within the carbon cycle and the exchange rates for CO_2 between these reservoirs.

DeVries (1958) first noticed some discrepancies between the radiocarbon and calendar ages of wood known to date from ca. A.D. 1700 and A.D. 1500. A correlation with climatic events was suspected particularly for the period referred to as the "little ice age." Using an electrical analog of Craig's (1957) ocean-atmosphere model DeVries found that a variation of 25% in the cosmic ray production rate was necessary to explain the observed changes in the specific activity of carbon-14 of 2% in the atmosphere. The same variation would have been produced by a change of about 25% in the exchange rate between the atmosphere and the deep ocean water through the surface layer of the ocean. If the variation was caused by a fluctuation in the exchange rate between the atmosphere and the surface layer of the ocean or between the surface layer and the deep ocean, each had to vary by nearly 50%. Independently, Stuiver (1961) pointed out

that the available carbon-14 data from wood of known age indicated a correlation between the carbon-14 inventory and solar activity. Recent measurements by Stuiver (1965) on material from the 18th and 19th centuries and by Suess (1965) on samples from the second millennium A.D. confirm this correlation. For older samples - up to 6000 years - the deviation between true and radiocarbon ages appears to be much larger. Tree rings, dated dendrochronologically and by radiocarbon, show deviations up to 15% with maximum differences being observed for samples about 4000 B.C., Damon (1965), Damon et al. (1966), Suess (1965) and Bien and Suess (1967).

Although historical records make it possible to retrace the magnitude of solar activity and sunspot numbers to the beginning of the Christian era, quantitative records of sunspot numbers date back only to the 17th century. Variations of carbon-14 activity can be determined as far back as dendrochronologically dated wood is available, and according to Ferguson (1968) this limit reaches 6700 B.P. for the species "Pinus aristata" - bristlecone pine wood. The carbon-14 measurements indicate that the solar-induced changes of 1-2% in carbon-14 specific activity (1 percent corresponds to about 80 years) are superimposed upon larger changes on a longer time scale. This appears to be true in particular for the last two or three millennia B.C., when the specific carbon-14 activity of the biosphere appeared to decrease steadily by ca. 0.4% per century, Damon et al. (1966).

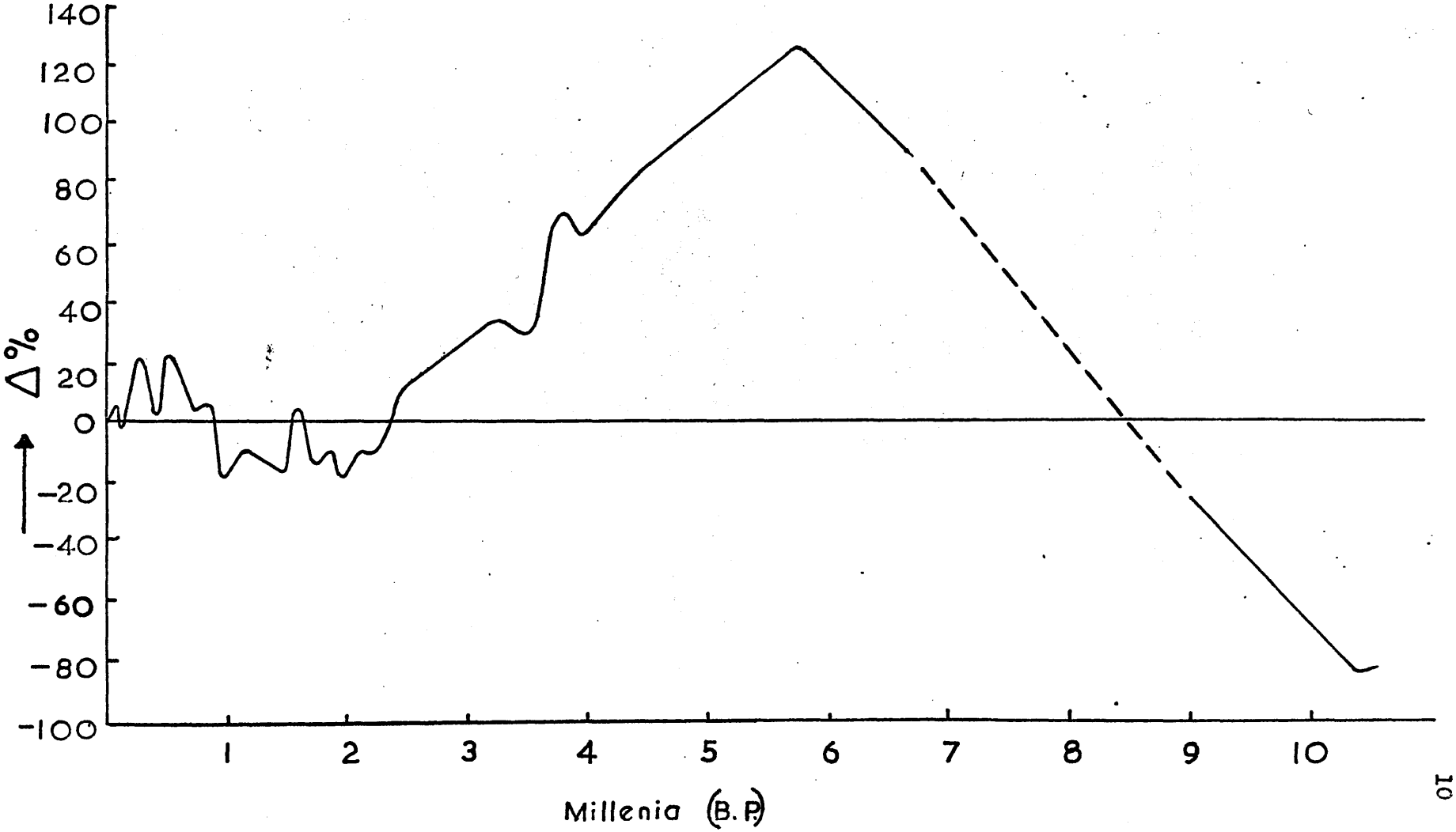
The causes of the long term variations of carbon-14 levels are not known. It is likely that the variations are partially the result of changes in the cosmic ray production rates of radiocarbon, but climatic conditions that affect ocean mixing and atmospheric CO_2 concentrations may also contribute. The cosmic ray flux, and hence the production rate of carbon-14, is a function not only of the solar activity but also of the magnetic dipole moment of the earth, and there are indications that the dipole moment may also have changed over the past 6000 years, Elsasser et al. (1956), Kigoshi and Hasegawa (1966), Libby (1965).

In general, radiocarbon dates from A.D. ~1000 to the present appear to be younger than the true age. A point of greatest deviation is around A.D. 1700 when radiocarbon ages erroneously suggest 19th century material. Radiocarbon dates from the first millennium A.D. to 300 B.C. appear 50 to 100 years too old. For the period before 300 B.C. radiocarbon ages are probably too young again (Figure 1.2).

A number of correction curves have been published but these must remain tentative, Suess (1965), Damon et al (1965, 1966), Kigoshi (1965), Stuiver (1965, 1967), Bray (1965), Stuiver and Suess (1966), Dyck (1965).

Radiocarbon data given in the literature are calculated with the so-called conventional Libby half-life of 5568 years. The average of the most recent measurements gives the more accurate value of 5730 $\pm$ 40 years, Mann et al (1961), Olsson et al (1962, 1963), Hughes et al (1963), Godwin (1962). Since

Figure 1.2. Variations of Atmospheric Carbon-14 Concentrations During the Last 12 Millenia (Damon 1965)



doubt still exists regarding the true half-life of carbon-14 the procedure for reporting ages relative to the 5568 year half-life value ensures comparibility of data.

1.3. Fluctuations of Environmental Radiocarbon Concentrations Caused by Artificial Effects.

Since 1900 mankind has upset the assumed steady state distribution of carbon-14 within the various carbon reservoirs in two ways: Firstly, the combustion of coal and oil has added a considerable quantity of carbon-14 - free CO_2 to the atmosphere. This has significantly reduced the carbon-14 specific activity in both the atmosphere and those reservoirs in rapid exchange with it (Suess Effect). Secondly, the testing of nuclear devices has added $^{14}CO_2$ to the atmosphere, thereby increasing the carbon-14 specific activity of the atmosphere and those reservoirs in rapid exchange with it (Bomb Effect).

1.3.1. Suess effect

This effect was first described by Suess (1953, 1954) following some measurements of the carbon-14 content of recently grown and 19th century wood samples. He found discrepancies in the carbon-14 specific activity of the modern samples amounting to about 2%, which were absent in the 19th century samples. These discrepancies he attributed to the assimilation by the biosphere of carbon-14 free CO_2 released to the atmosphere by the combustion of fossil fuels. Such an effect, being directly

related to industrial activity, therefore became apparent in the northern hemisphere with the onset of industrial revolution.

Revelle and Suess (1957) have estimated the quantity of CO_2 that has been added to the atmosphere by combustion of fossil fuels for each decade since 1860 (beginning of the industrial revolution). They showed that in 1870 the cumulative amounts corresponded to about 0.23% of the natural CO_2 present in the atmosphere, in 1910 to about 1.9%, and in 1960 to 15.6%. Measurements of atmospheric CO_2 concentrations demonstrate, however, that there has not been a corresponding increase. Most of the excess CO_2 from combustion of fossil fuels must therefore have been transferred to the oceans. The rate of this transfer is not firmly established and previous estimates for this exchange time range from 16 hours, Dingle (1954), to the order of 1000 years, Plass (1956).

The decrease in the natural carbon-14 concentration by industrial fuel combustion over the past 100 years was estimated to be between 2% and 6% for the northern hemisphere, Houtermans and Suess (1967), and less than 1% in the surface layer of the ocean, Broecker et al (1960).

The interpretation of the Suess Effect in the southern hemisphere is less clear because of lack of data. Due to inter-hemispheric atmospheric mixing time the average Suess Effect in the southern hemisphere should be smaller than that in the northern hemisphere.

Variations in the CO_2 concentration in the atmosphere have been investigated by many workers since the early 19th century

using a variety of analytical methods. The majority of data range between 270 and 350 p.p.m. by volume. Recently, Bolin and Keeling (1963) have made a comprehensive survey of atmospheric CO_2 concentrations and found an average value to be 314.5 p.p.m. in January 1960, with a rate of increase of approximately 0.72 p.p.m. annually. It was also found that the geographical variation did not exceed 6 p.p.m., the maximum being in the northern high latitudes and the minimum being in the southern high latitudes.

Since the Suess Effect has led to a decrease in the carbon-14 specific activities in the atmospheric and biospheric reservoirs, the choice of such carbon as a primary standard in radiocarbon dating would give rise to young ages. To avoid this possibility the primary standard activity used is that of age-corrected 19th century wood.

An important consequence of the Suess Effect could be, in the long-term, an elevation of the atmospheric temperature. Plass (1956) calculated that a 10% increase in the atmospheric CO_2 would increase the average temperature by 0.36°C.

1.3.2. Bomb effect

Over the past decade considerable amounts of carbon-14 have been released to the atmosphere during nuclear weapons tests. The carbon-14 is produced by the free neutrons which escape from the exploding nuclear devices and are subsequently absorbed by atmospheric nitrogen. The production of carbon-14 will depend on the type and power of nuclear device exploded, and

will also depend on whether the explosion occurred at the surface of the earth or high in the atmosphere. A surface test will produce approximately 50 percent of the carbon-14 produced by a similar device in air test since one half of the escaping neutrons will be captured in the earth rather than by the atmosphere. Practically all the neutrons escaping from the exploding nuclear device to the atmosphere are expected to produce carbon-14, Machta (1959). It appears reasonable to assume also that this carbon-14 is soon converted to $^{14}CO_2$ which will then move upwards with the hot gases from the explosion. The published energy yields of nuclear devices tested during the period 1945-1962, together with an estimate of the yields for the period 1962-1968 are presented in Table 1.1.

Estimates of carbon-14 production in relation to energy yield that have appeared in the literature range from 4.5×10^{25} atoms/Mton fission, Libby (1956), to 14×10^{26} atoms/Mton fusion, Leipunsky (1957). The most accepted figures for carbon-14 production in the atmosphere are 2×10^{26} atoms/Mton of total (fission and fusion) energy yield in the case of an air burst and 1×10^{26} atoms/Mton for a surface burst, Machta (1959). On this basis the total production of carbon-14 to date is therefore estimated at about 1×10^{29} atoms, i.e., sufficient to raise the carbon-14 concentration by almost a factor of four were it to be contained in the troposphere.

The first experimental verification of increased atmospheric carbon-14 levels due to nuclear testing was reported by Rafter and Fergusson (1957). Subsequently this increase has been

Table 1.1. Fission and fusion energy yields

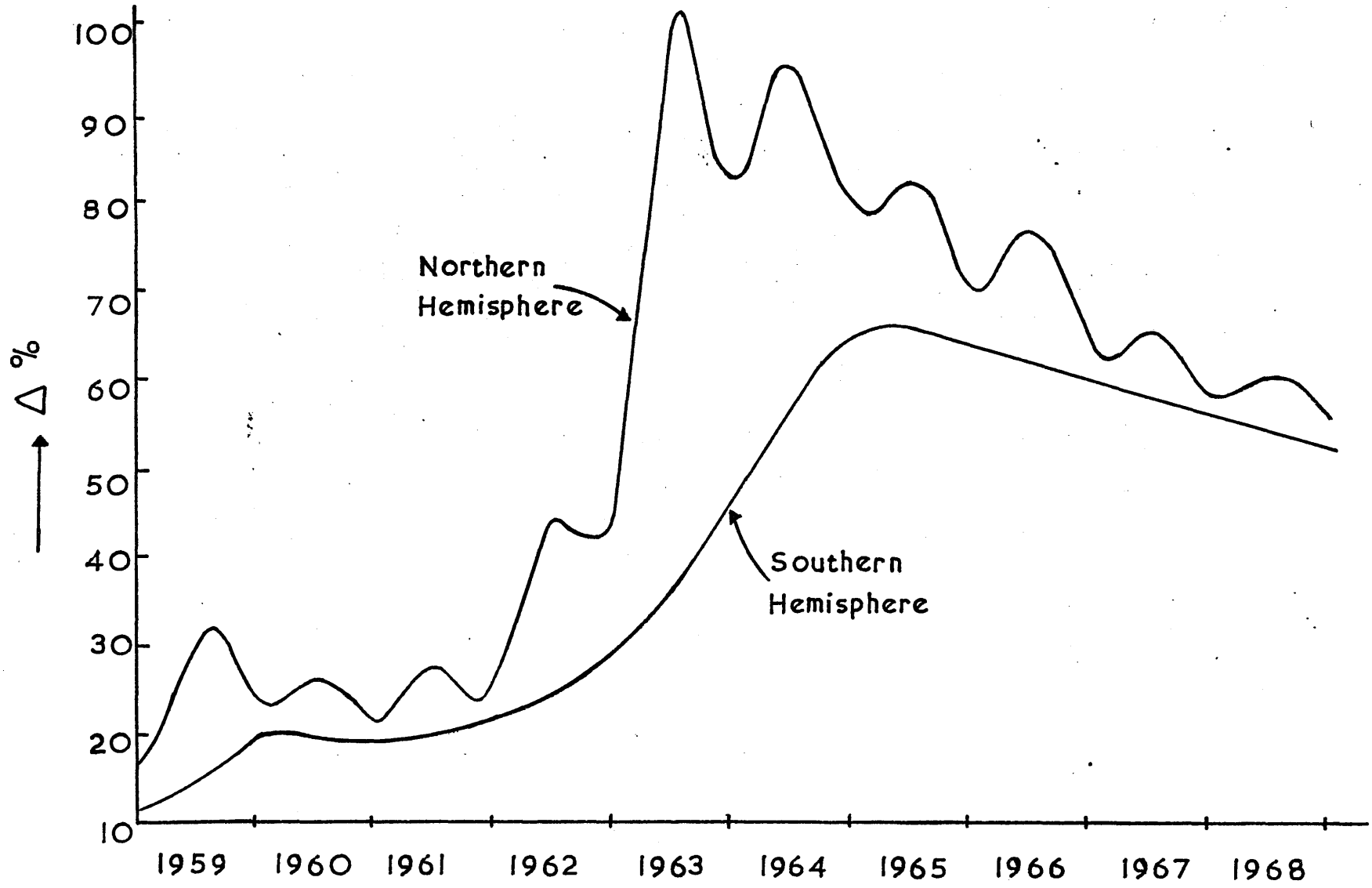
Period	Fission yield (Mton)		Fusion yield (Mton)	
	Air tests	Surface tests	Air tests	Surface tests
1945-51	0.19	0.57	-	-
1952-54	1.0	37.0	-	22.0
1955-56	5.6	7.5	5.4	9.5
1957-58	31.0	9.0	26.0	19.0
1959-60		Test	Moratorium	
1961	25.0	-	95.0	-
1962	76.0	-	141.0	-
1963-68	0.3	0.1	15.0	-
Total	139.09	54.17	282.4	50.5

followed by various workers, including Broecker and Walton (1959), Broecker and Olson (1960), Nydal (1963), Münnich and Vogel (1963), Nydal and Lövseth (1965) and Olsson et al (1967).

During mid-1963, the largest tropospheric injection of man-made carbon-14 occurred in the high northern latitudes, principally as a result of the U.S.A. and U.S.S.R. tests of 1961 and 1962. This activity was introduced into the stratosphere predominantly at 50° - 75° N and gave rise to peak intensities about 100% above the normal level in the spring and early summer of 1963, one year after the extensive test series. This delay arose from the internal mixing rates of the stratosphere and the seasonal nature of stratospheric - tropospheric mixing. Since the cessation of the major nuclear test series the carbon-14 activity in the northern hemisphere troposphere has continued to decrease following the 1963 peak due to inter-hemispheric mixing and the absorption of $^{14}CO_2$ by the ocean and biosphere.

In the southern hemisphere troposphere the increase in carbon-14 concentrations has been relatively slow due to the time required for transport from the northern hemisphere, and the larger exchange of CO_2 between the oceans and the atmosphere in southern latitudes. The summer peaks observed in the northern hemisphere are less pronounced in the southern hemisphere (Figure 1.3.). The excess carbon-14 reached its maximum value in the southern hemisphere troposphere during mid-1965 with a value of about 65% above the normal level.

Figure 1.3. Carbon—14 Concentrations in Atmospheric CO_2, 1959—1969



At the present time (1969) the carbon-14 concentrations in the northern hemisphere troposphere (as found in this study) have decreased to an excess of about 56% above the normal level being 5% higher than that in the southern troposphere. This difference will diminish in a few more years as a result of interhemispheric exchange patterns. On the other hand the carbon-14 concentrations in the surface waters of the oceans have risen to about 15% above the normal pre-bomb value.

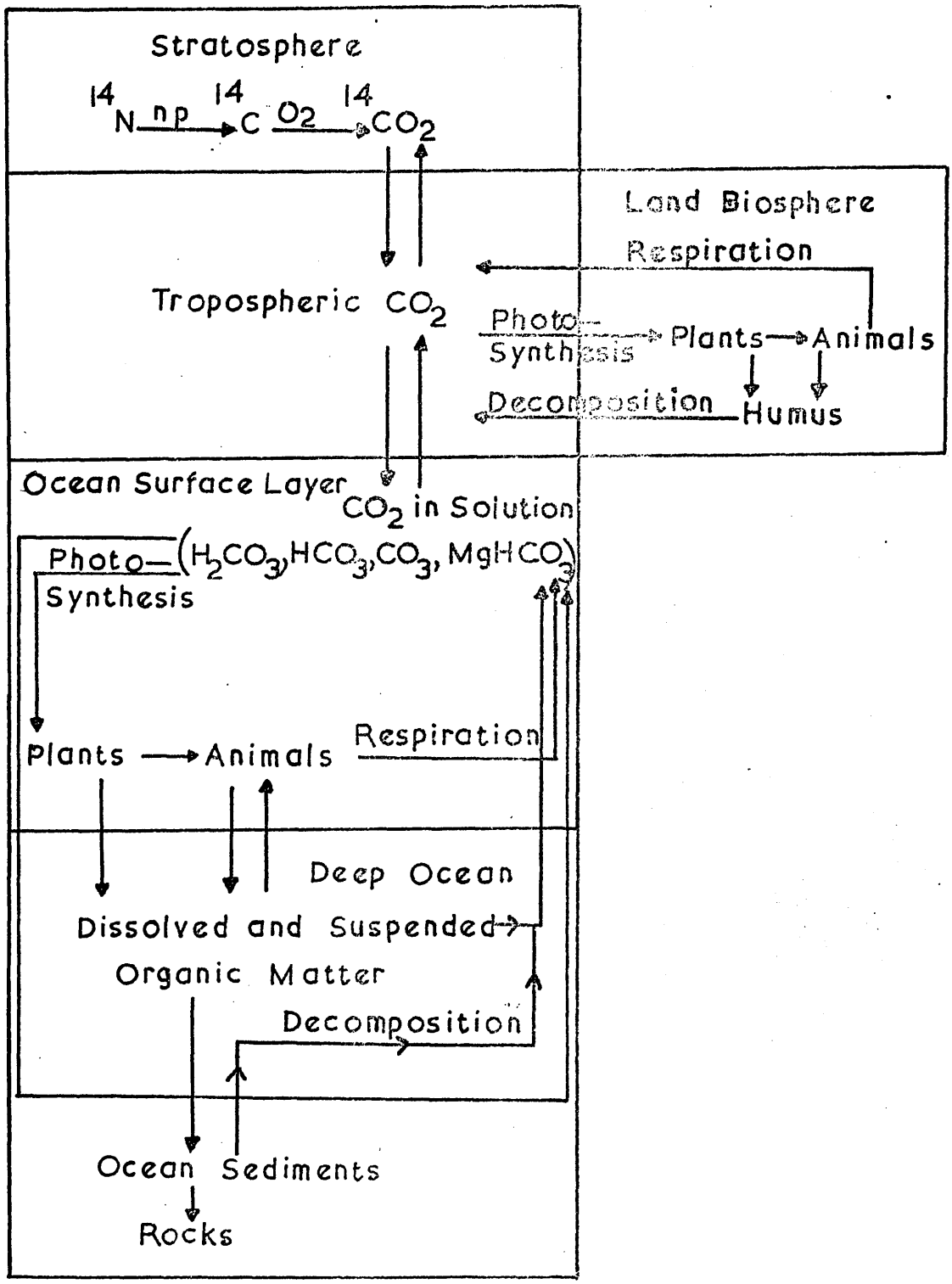
These additional data for the distribution with time of bomb-produced carbon-14 in the various reservoirs of the carbon cycle are valuable in the computation of more accurate values for the exchange parameters involved.

1.4. Carbon Cycle in Nature

The study of the carbon cycle in nature has attracted increasing attention due to its significance in geochemical, meteorological, biological and oceanographic problems. A change in the CO_2 concentrations in the atmosphere, for example, could appreciably affect the thermal budget of the surface of the earth, and might cause a long-term change in the climate due to the "greenhouse effect." It could also affect biological productivity and various geological phenomena such as the rate of erosion, and the chemical properties of ocean water.

In the natural carbon cycle (Figure 1.4) CO_2 is the medium for the transportation and exchange of carbon because of its stability and distribution in the atmosphere, hydrosphere and lithosphere. CO_2 from the atmosphere is being continually

Figure 1.4. The Carbon Cycle



transferred to the biosphere by photosynthesis while, concurrently, the atmosphere is being replenished by the oxidation of organic debris and the respiration of animals. Atmospheric CO_2 is in direct exchange with the dissolved CO_2 in the hydrosphere via molecular exchange through the interface between those reservoirs. It is therefore clear that radioactive carbon-14 can move freely between these various reservoirs but at a rate controlled by the movement of CO_2.

The estimated mass of carbon in each reservoir is summarized in Table 1.2. For the atmosphere and total ocean the accuracy is better than $\pm$ 5%. while for the biosphere, humus and surface water of the ocean a considerable error, possibly a factor of two, may be involved. It can be seen from Table 1.2 that the CO_2 content in the atmosphere, the smallest of all carbon reservoirs, may be strongly influenced by slight changes in the dynamic balance between the various reservoirs.

The mechanism for solubility of CO_2 in seawater is complex, the rate and extent of retention being sensitive functions of temperature, hydrostatic pressure, partial pressure of CO_2 in both the gas and liquid phases, mixing pattern of ocean water, etc. Therefore the exchange rate pattern is variable with geographical location. Various workers have investigated these factors, Takahashi (1961), Eriksson (1963), Kanwisher (1963).

From considerations of the steady-state carbon-14 distribution in the various exchangeable reservoirs of the carbon cycle, and using the naturally or artificially produced carbon-14, the rates of exchange of CO_2 between those reservoirs have been estimated

Table 1.2. Carbon content of various reservoirs

Reservoirs	Mass of Carbon (10^{17}g)	References
Atmosphere	6.57	Takahashi (1961)
Stratosphere	1.05	
Troposphere	5.52	
Hydrosphere	379.16	Broecker and Olson (1960)
Surface layer	8.16	" " " "
Deep ocean	371.0	" " " "
Biosphere (land)	8.34	Lieth (1963)
Terrestrial	1.24	" "
Humus	7.10	" "

by several investigators, Craig (1957), Revelle and Suess (1957), Rafter and Fergusson (1958), Broecker et al (1960), Lal and Rama (1966), Münnich and Roether (1967), Nydal (1967, 1968), Young and Fairhall (1968).

1.5. The Purpose of This Study

Although a number of workers have investigated the exchange rate of CO_2 between the various reservoirs of the carbon cycle there remains considerable uncertainty in the values of these parameters, e.g., recent results ranging from 2 to 25 years have been determined for the residence time of CO_2 in the atmosphere (Table 1.3). Our knowledge of geographical and temporal variations of $^{14}CO_2$ in the CO_2 cycle in nature remains incomplete.

The cessation of large-scale nuclear tests in 1963, however, has presented a unique opportunity for the study of exchange rates between the dynamic carbon reservoirs since the change of carbon-14 concentrations in these reservoirs is controlled only by the exchange rates. The objective of this research, therefore, is to study the following parameters, making use of the bomb-produced carbon-14 as a tracer:

1) Rate of mixing within the stratosphere and between the stratosphere and troposphere.
2) Rate of mixing of tropospheric air masses across the equator.
3) Rate of exchange of CO_2 between the troposphere and ocean surface layer.

Table 1.3. The mean residence times (years) of CO_2 in various reservoirs.

Authors		Basis for estimate	st*	ss	tt	tm
Arnold and Anderson	(1957)	Natural C-14				10-20
Arnold and Anderson	(1957)	Suess effect				20
Revelle and Suess	(1957)	Suess effect				10
Craig	(1957)	Natural C-14			2-5	7± 3
Fergusson	(1957)	Suess effect			1.8	2-10
Munnich and Vogel	(1958)	Bomb C-14			1-2	
Rafter and Fergusson	(1958)	Bomb C-14				3.3
Hagemann et al.	(1959)	Bomb C-14	5			
Broecker and Walton	(1959)	Bomb C-14		1	1	
Bolin and Erickson	(1959)	Suess effect				5
Broecker and Olson	(1960)	Bomb C-14				4**
Junge	(1961)	Suess effect			2-3	
Junge	(1962)	Annual cycle of CO_2			0.9	
Munnich and Vogel	(1963)	Bomb C-14		5	1	
Bolin and Keeling	(1963)	Annual cycle of CO_2			0.9	
Feely et al.	(1966)	Bomb C-14	1.5			
Lal and Rama	(1966)	Bomb C-14	0.8 + 0.3 - 0.2		1.2	4

Table 1.3. (continued).

Authors		Basis for estimate	st*	ss	tt	tm
Munnich and Roether	(1967)	Bomb C-14				5.4
Bien and Suess	(1967)	Bomb C-14				25
Nydal	(1967)	Bomb C-14	3.5 ± 0.8	3-5	0.5 ± 0.2	
Young and Fairhall	(1968)	Bomb C-14	1.5			2.5
Nydal	(1968)	Bomb C-14	2.0 ± 0.5	5.0 ± 1.5	1.0 ± 0.2	5-10

* st = Residence time of CO_2 in the stratosphere before transfer to the troposphere.
ss = Residence time of CO_2 in the northern hemisphere stratosphere before transfer to the southern stratosphere.
tt = Residence time of CO_2 in the northern hemisphere troposphere before transfer to the southern troposphere.
tm = Residence time of CO_2 in the troposphere before transfer to the ocean mixed layer.

** The computation was based on the assumption that stratospheric mean residence time is five years.

4) Rate of mixing of ocean surface water through the thermocline into deeper layers of the ocean.

5) Latitudinal distribution and seasonal variation of $^{14}CO_2$ in the troposphere.

The following areas indicate where results from present work will be applicable:

(1) Knowledge of the isotopic exchange rate between atmospheric CO_2 and the oceans is required for an interpretation of the secular variations in the natural cosmic ray produced carbon-14.

(2) The continued addition of CO_2 to the atmosphere by the combustion of fossil fuel may lead to an increase in the CO_2 content of the air, large enough to affect the terrestrial climate. If, and when, this will be the case can only be determined by careful study of the rate of uptake of CO_2 by the oceans.

(3) Simultaneous measurement of the atmospheric carbon-14 levels at various worldwide locations will allow a better understanding of the mechanisms involved in CO_2 transfer across reservoir boundaries, and of atmospheric mixing patterns.

(4) Monitoring the tropospheric carbon-14 levels during the period of bomb carbon-14 production allows application of short term dating to materials in exchange with the tropospheric reservoir during this time.

CHAPTER 2: EXPERIMENTAL PROCEDURES FOR CARBON-14 ASSAY

The measurement of natural radiocarbon is a rather specialized technique with respect to both the chemical and physical procedures which must be employed. This is due to the very low specific activity of carbon-14 present in contemporary samples, viz., 6.3 pc/g carbon, coupled with the weak energy (0.155 MeV) of the beta particles emitted during the carbon-14 decay. The former characteristic requires the use of relatively large samples, with particular care being necessary to avoid contamination by environmental carbon, and the latter severely limits the methods which can be employed for radiometric measurement. The following resume of technique employed to date will serve to underline the nature of the experimental difficulties involved.

Anderson and Libby (1951) and Libby (1955) were the first to describe a system suitable for measuring the natural carbon-14 activity in environmental samples. The sample preparation involved conversion of the carbon atoms in the sample to carbon black which was then coated on to the inner surface of a metal cylinder. This cylinder was placed around a Geiger tube modified so that the normal cathode (wall) was replaced by a wire grid, thus dispensing with the problem of end window absorption. The effective geometry of this arrangement was about 50% and the large surface area of the sample compensated in part for the loss of counts by self absorption in the carbon

sample. The counter accommodated 8g of carbon over an area of 400cm^2 and an absolute counting efficiency of 5.4% for carbon-14 was achieved.

As the solid carbon preparation was very susceptible to absorption of radioactive gases and dust from the atmosphere the risk of contamination was so great that it has been almost impossible to make determinations with this method since large scale testing of nuclear devices began in 1951. Other objections to this technique were that the chemical treatment required rather a long time and that fairly large quantities of carbon were needed. Also since the carbon-14 β^- particle has a range of only 28mg/cm^2 in aluminium, great care was necessary to ensure an even thickness of the carbon deposit.

These drawbacks caused several investigators to develop new techniques for radiocarbon studies. The use of Geiger counters filled with a mixture of CO_2 + CS_2 was reported by Crane (1954) and Moscicki (1958). Efficiencies for these systems reached 70-80%. Low background proportional counters using CO_2, C_2H_2, CH_4 or C_2H_6 as the counting gas have been described by DeVries and Barendsen (1952), Fergusson (1955), Olsson (1958), Suess (1954), Burke and Meinschein (1954, 1955), and Faltings (1952). In the early attempts poor counting characteristics were ascribed to CO_2 but later it was shown by Fergusson (1955) that electronegative impurities in the gas were the cause of the difficulties. At gas filling pressures of greater than 1 atm., the background counting rate increases markedly when electronegative impurities are present and plateau

lengths decrease considerably. Oxygen is one of the most common contaminants (one can tolerate only about 1 x 10^{-3}mm partial pressure in three atm.); others include water, ammonia and hydrogen chloride.

Gas proportional counters have a counting efficiency of approximately 100% compared to about 5% for the solid sample counters. They are also free from the hazard of airborne contaminants and can be used for as little as 0.1g of sample carbon.

The incorporation of a carbon compound into a scintillation liquid was first reported by Hayes, Anderson and Arnold (1955). Liquid scintillation techniques have the great advantage that the total volume of the counting medium is small and the sample is in a condensed phase with a corresponding density many times greater than that of gases. Massive shielding and the use of anticoincidence shields are not necessary as the cosmic ray particles (mesons) give large pulses in a liquid scintillation and can be easily discriminated against by pulse height selection. The background is mainly determined by the dark current of the phototube which may be rather high for the energies of carbon-14 measurement. While these problems can possibly be overcome by the choice of carefully matched photo-multipliers and stable electronics in conjunction with coincidence circuitry there remains the rather complex synthesis of the sample into a form convenient for incorporation into the liquid scintillator. This process does not normally result in 100% yields, and thus the possibility of isotopic fractionation arises. Barendsen

(1957) has overcome some of these difficulties by using liquid CO_2 as a diluent.

This study required a technique capable of handling the analysis of a large number of samples for their carbon-14 content. Such a system has been constructed in which the samples are converted first into CO_2 and then into CH_4 for gas proportional counting.

CH_4 was chosen as the counting gas because of the advantages it possesses over two of the alternative counting gases used in carbon-14 dating - CO_2 and C_2H_2. It is not subject to the stringent purity requirements of CO_2 and in fact Diethorn (1956) states that up to 0.35% air can be present without affecting its counting characteristics. Secondly, in its explosive tendencies CH_4 presents much less danger than C_2H_2. The presumed advantage of C_2H_2 in having twice the molecular carbon content of CH_4 is offset by the fact that CH_4 can be counted at much higher filling pressures.

As to the synthesis of CH_4 for carbon-14 dating, at least two different chemical methods have been reported. Burke and Meinschein (1955) described a catalytic hydrogenation technique involving the reaction $CO_2 + 4H_2 \longrightarrow CH_4 + 2H_2O$, over a ruthenium catalyst maintained at 475°C. A conversion efficiency of 99% was achieved in the synthesis of tenth molar quantities of CH_4. The alternative batch reactor method of Fairhall, Schell and Takashima (1961) involves the use of a stainless steel high pressure reactor fitted with two side arms for the condensation of reactants and products. The reactor is filled with the CO_2

to be converted and the H_2 added in two stages. Overall yields of approximately 98% are achieved and the CH_4 is free from CO and CO_2. Olson and Nickoloff (1965) have described a modification of the system designed by Fairhall et al. (1961).

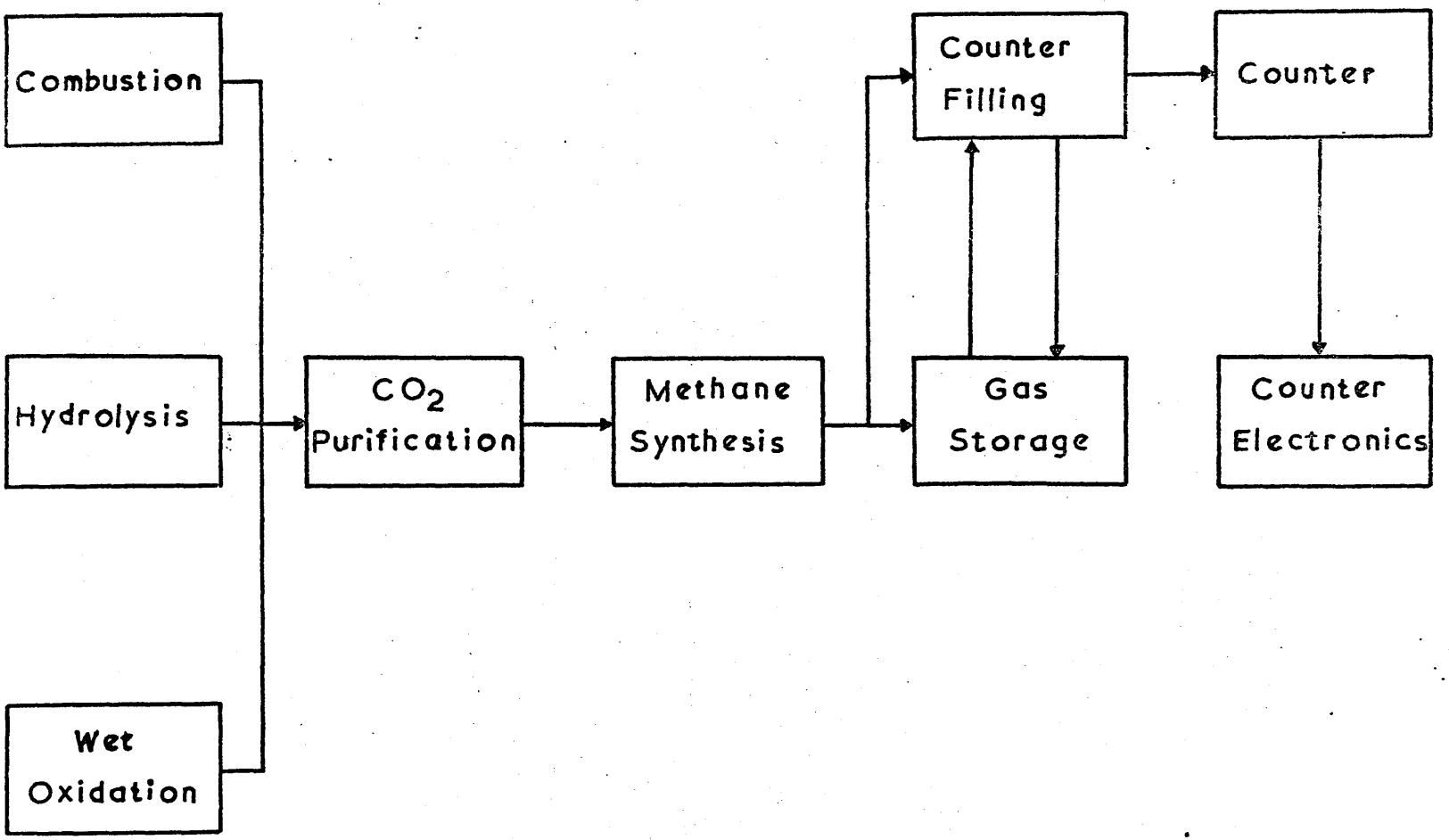
In this research a new flow system has been designed and used successfully for CH_4 synthesis, (a highly modified form of the one in use at the I.A.E.A.'s Radiocarbon Laboratory in Vienna). The system is constructed almost entirely from glass and has the advantage that it is operated at less than 1 atm. pressure. A catalyst of ruthenium on alumina, maintained at a temperature of 350°C, is utilized and a diaphragm pump is used to circulate the mixture of gases, $CO_2 + H_2$, through the catalyst.

A proportional gas counter is used for counting (Beckman Instruments Ltd., Glenrothes).

A high vacuum throughout the system is attained with a mercury diffusion pump backed by a rotary oil pump. A second rotary pump is available for rough pumping. The complete system is shown diagramatically in Figure 2.1.

The pretreatment of most samples to be assayed for carbon-14 is considered essential for the removal of any contamination by foreign carbon material. In the case of atmospheric CO_2 samples special attention must be given to the choice of sampling site to avoid the possibility of contamination by fossil fuel CO_2 during sample collection.

Figure 2.1. Block Diagram of Procedures for Carbon-14 Assay



2.1. Chemical Procedures for Carbon-14 Assay

Since all natural radiocarbon measurements begin with CO_2 gas a method for the preparation of pure CO_2 from a variety of starting materials is required. Further treatment of the CO_2 varies according to the type of counting gas selected. In the following section the sample collection, pretreatment of various materials and the preparation of the counting gas are discussed.

2.1.1. Collection of samples and their pretreatment

Atmospheric CO_2 samples were collected by employing a static technique to give cumulative monthly collections. Aqueous solutions of carbonate-free 8N KOH were exposed to the atmosphere whereby CO_2 was absorbed and retained in the solution as carbonate.

Prior to the routine collection of the atmospheric samples the following preliminary tests were carried out to determine the best conditions for CO_2 collection. 250ml of 0.5N, 2N, 4N and 8N carbonate-free KOH solutions were exposed to the atmosphere in polythene dishes on the roof of the University building for two weeks. After the exposure period the samples were treated by the following method to precipitate the CO_2 absorbed as $BaCO_3$: 5N $BaCl_2$ solution was added to the exposed KOH solution stirring after each addition and slightly heating to help precipitation. When precipitation was complete 2ml of $BaCl_2$ solution were added in excess. The $BaCO_3$ was then filtered through a Whatman No. 50 filter paper and the precipitate washed

well with warm distilled water to remove any $Ba(OH)_2$. The $BaCO_3$ was dried in a moderate oven (100°C) and then weighed.

The experimental results obtained with different strengths of KOH solution are shown in Table 2.1. It had already been decided to operate on a monthly collection basis, and maximum sample size was required to allow a second measurement of any collection period should this appear necessary (50g $BaCO_3$ per determination). The results showed similar collection efficiencies for 4N and 8N KOH solutions over the 14 day test period. Over longer periods, however, it was likely that the 4N solution would become saturated and therefore it was decided to use 8N solutions on a routine basis. Exposure of solutions of greater than 8N proved impractical due to a rapid formation of crystalline K_2CO_3 over the exposed solution.

The 8N KOH solutions were prepared from freshly distilled water and tested for carbonate by addition of saturated $BaCl_2$ solution before forwarding them to the sampling stations in a sealed polythene bottle. On return to the laboratory the carbonate formed during the exposure was precipitated as $BaCO_3$, filtered, dried and weighed in the manner described previously. Finally the $BaCO_3$ was crushed and stored in a screw-cap bottle.

The carbonaceous materials to be subjected to carbon-14 measurement were treated according to their nature. Most organic samples were first leached in dilute HCl to remove any carbonate. In some cases dilute NaOH was used to remove possible contamination with humic materials. After leaching, the sample was washed and dried, and was then ready for combustion.

Table 2.1. Efficiency of CO_2 absorption as a function of KOH concentration (250ml of KOH exposed for 14 days).

Strength of KOH solution	Weight of $BaCO_3$ precipitate (g) Exp.1	Exp.2	Exp.3	Mean
0.5N	9.35	9.06	7.88	8.76
2 N	36.51	38.35	36.69	37.18
4 N	55.53	67.89	58.17	60.53
8 N	59.27	62.64	60.84	60.92

Shells were generally washed in dilute acid for a short time to remove the outer layers of material which may have been contaminated with more recent carbonate.

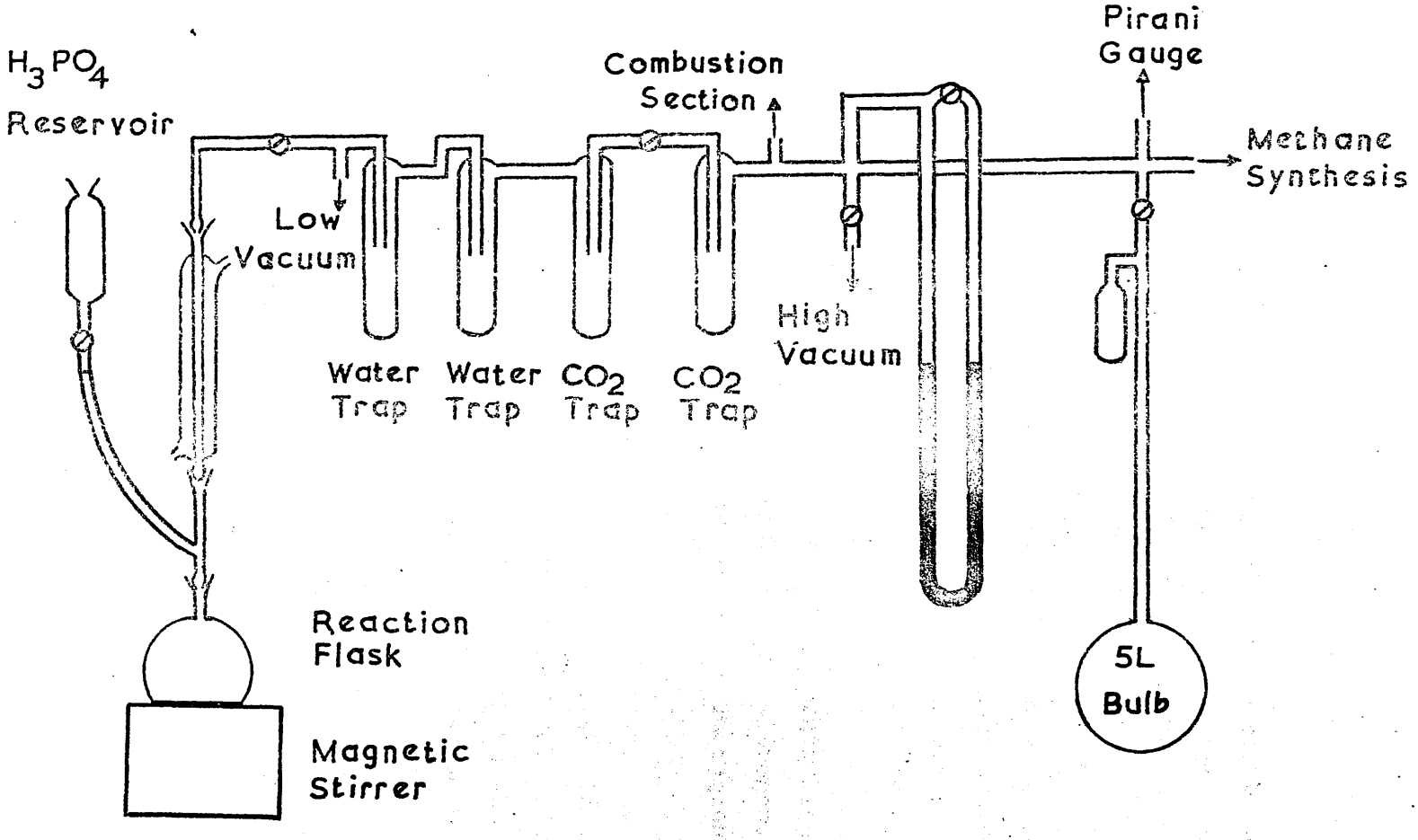
In this laboratory the basic pretreatment of wood, peat. and charcoal samples consists of visual examination for intrusive rootlets followed by boiling successively in distilled water, 5% HCl, and distilled water, 5% NaOH, distilled water, 5% HCl, and distilled water. Shells and marble samples are leached in 5% HCl to remove 20% by weight, and then washed with distilled water. Collection of atmospheric CO_2 samples and their pretreatment have already been described.

2.1.2. Preparation and purification of CO_2 gas

After any necessary pretreatment carbonate materials are hydrolysed using 50% phosphoric acid solution (Figure 2.2).

The sample is placed in a flask fitted with an adaptor to allow the entry of acid and the exit of gases. After the apparatus has been assembled and evacuated, a 50% solution of phosphoric acid is slowly admitted from the reservoir. The contents of the flask can be magnetically stirred to aid the reaction. The CO_2 released is first passed through a water-cooled condenser and two cold traps cooled ($-79^{\circ}C$) by dry-ice to eliminate any water vapour present, and then condensed in two consecutive traps cooled by liquid nitrogen ($-196^{\circ}C$). When the reaction is complete the traps with the condensed CO_2 are separated from the rest of the system by closing the

Figure 2.2. Hydrolysis Section



appropriate stopcocks and then pumped to a high vacuum (< 1 micron), so that all gases that have an appreciable vapour pressure at -196°C are removed. Occluded gases can be removed by sublimating the CO_2 once or twice more. Finally the purified CO_2 is transferred to a 5 l volume-calibrated bulb for yield determination.

The results of ten successive efficiency experiments are shown in Table 2.2. Yields in all cases range between 96-100% with an average value of 98.7%. High efficiency is desirable in this process to minimize the possibility of isotopic fractionation.

Organic carbon is converted to CO_2 by controlled combustion in a mixed gas stream comprising oxygen and nitrogen. Figure 2.3 shows the apparatus used for combustion and subsequent purification of the CO_2 gas.

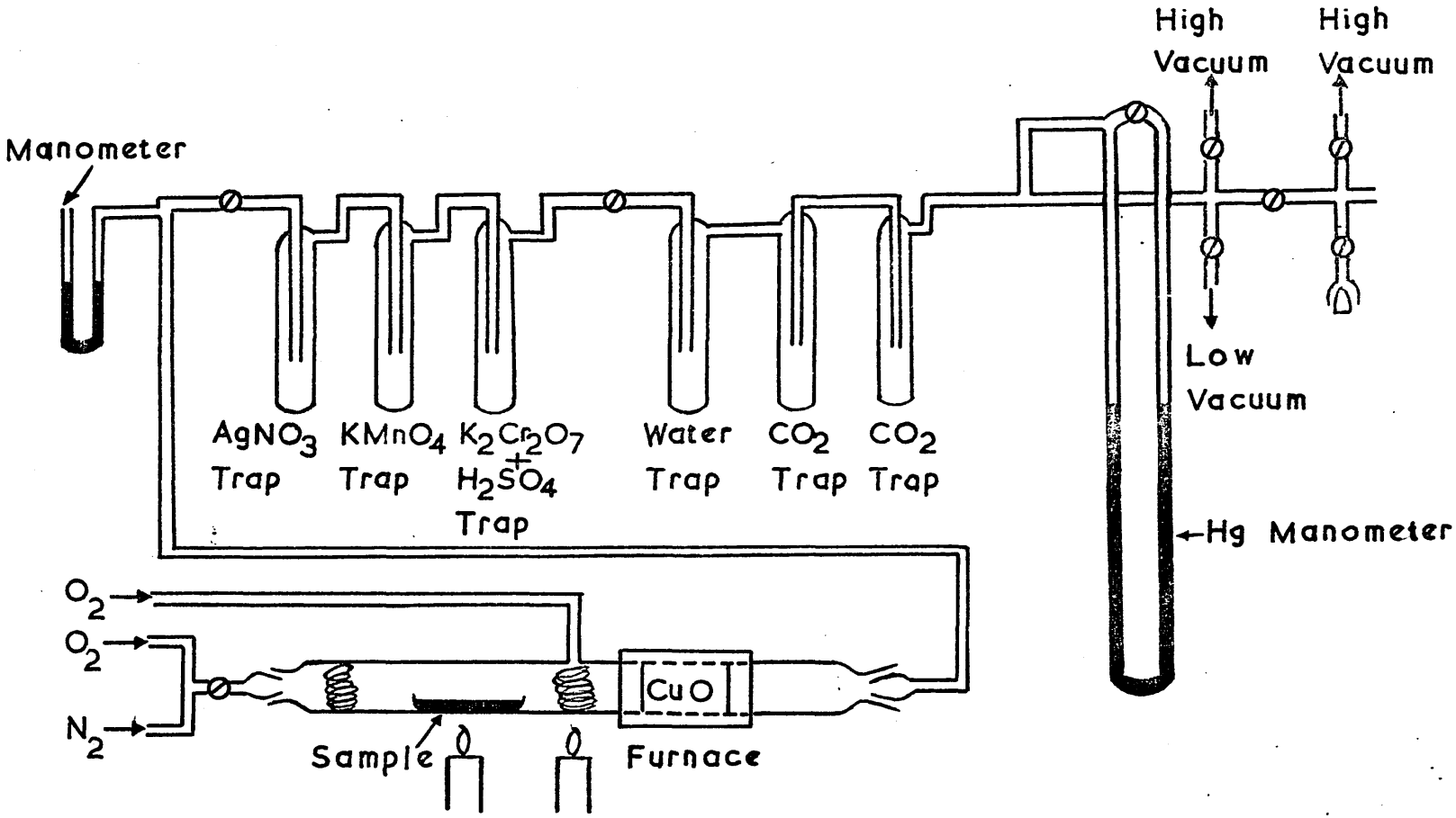
Organic samples are introduced into the first half of the silica combustion tube (about 3.5cm in diameter and 65cm long). Copper oxide (CuO) is packed into the second half of the tube about 15cm in length. Before combustion begins the CuO is heated to redness (~550°C) and a mixture of oxygen and nitrogen is passed through the system at a controlled flow rate. The flow of the gases is further controlled by pulling a slight vacuum through the system. The sample is gently heated by a Meker burner until combustion begins.

Initially only one oxygen entry to the silica combustion tube was employed and two of the early experiments resulted in minor explosions. It was assumed that this was due to rapid

Table 2.2. Efficiency of hydrolysis

The amount of sample ($BaCO_3$)g.	Amount of CO_2 expected	1-atm obtained	Yield %
45.0	5.11	5.05	98.8
50.0	5.68	5.68	100.0
41.9	4.76	4.61	96.8
53.0	6.02	5.97	99.2
52.0	5.90	5.90	100.0
52.5	5.96	5.73	96.1
56.0	6.36	6.26	98.4
55.0	6.24	6.24	100.0
55.0	6.24	6.11	97.9
53.0	6.02	6.02	100.0
		Average	98.7

Figure 2.3. Combustion and Purification System for CO_2 Gas



oxidation of the tar materials formed initially when the organic sample is heated. Addition of a second oxygen inlet and a decreased oxygen flow over the sample helped to overcome this problem. Oxygen enters the second inlet in the combustion tube prior to the CuO furnace in order to burn the volatilized carbon materials. Adjustment of the heating rate, so that a high pressure is not allowed to build up inside the combustion tube also helps to avoid explosions. The pressure change within the system can be monitored by the manometer situated after the combustion tube.

The flow rates of oxygen in the side arm and nitrogen are held at about 600ml/min. and 500ml/min. respectively throughout the combustion. The flow rate of oxygen over the sample is adjusted to about 100ml/min. at the beginning and is raised to 400ml/min. towards the end of the combustion. These flow rates are subject to slight modification, however, according to the type of sample.

The combustion products, mainly CO_2 with some water vapour and perhaps some HCl, NO, NO_2 and SO_2, are passed through a series of bubblers containing (1) an aqueous solution of $AgNO_3$, (2) acidic $KMnO_4$, and (3) H_2SO_4 saturated with $K_2Cr_2O_7$.

The first bubbler contains 0.5 N $AgNO_3$ solution which removes halogens from the gas. The second bubbler contains acidic (H_2SO_4) $KMnO_4$ which absorbs sulphur dioxide and some oxides of nitrogen, and the third bubbler contains concentrated H_2SO_4 saturated with $K_2Cr_2O_7$ which removes water vapour and sulphur dioxide. The CO_2 gas is then passed through a trap

cooled by dry-ice and condensed in two successive traps cooled by liquid nitrogen. These traps are pumped to high vacuum as described above and then the CO_2 is transferred to 5 l calibrated bulb.

In some cases a blue colour was observed in the CO_2 produced on combustion. This has also been reported by DeVries (1955). It is possible that the oxides of nitrogen are not effectively absorbed by the $KMnO_4$ solution, and condensed with the CO_2 in the liquid nitrogen trap. The blue colour could arise from nitrogen trioxide (N_2O_3) in equilibrium with the other oxides of nitrogen, i.e., $NO + NO_2 \rightleftharpoons N_2O_3$. Distillation of the CO_2 at -196°C removes the bulk of this contaminant. The small percentage remaining is passed to the CH_4 synthesis stage with the CO_2, where, presumably the nitrogen oxides are reduced to NH_3 which being soluble in water is removed as NH_4OH in the water trap. Experience has shown that this secondary reaction is not detrimental to the overall CH_4 synthesis, and the possibility of poisoning of the catalyst has not been noted.

A series of efficiency experiments yielded the results shown in Table 2.3.

Wet oxidation is used to produce standard carbon-14 labelled gas for counter calibration. The apparatus used is the same as in Figure 2.2.

Carbon-14 labelled oxalic acid, obtained from the National Bureau of Standards, is oxidized using acidic $KMnO_4$ solution. The CO_2 released from oxidation is purified by distillation and passed into the calibrated 5 l bulb. The efficiency of this method is shown in Table 2.4.

Table 2.3. Efficiency of CO_2 production by combustion

Sample g.	Amount of CO_2 1-atm expected	obtained	Yield %
12.51 (O)[x]	4.45	4.16	93.5
14.00 (O)	4.98	4.54	91.2
7.80 (O)	2.77	2.61	94.2
3.35 (B)[xx]	4.30	3.92	91.2
3.67 (B)	4.71	4.31	91.5
3.13 (B)	4.02	3.97	98.8
		Average	93.4

[x] (O) - Oxalic acid

[xx] (B) - Benzoic acid

Table 2.4. Efficiency of CO_2 production by wet oxidation

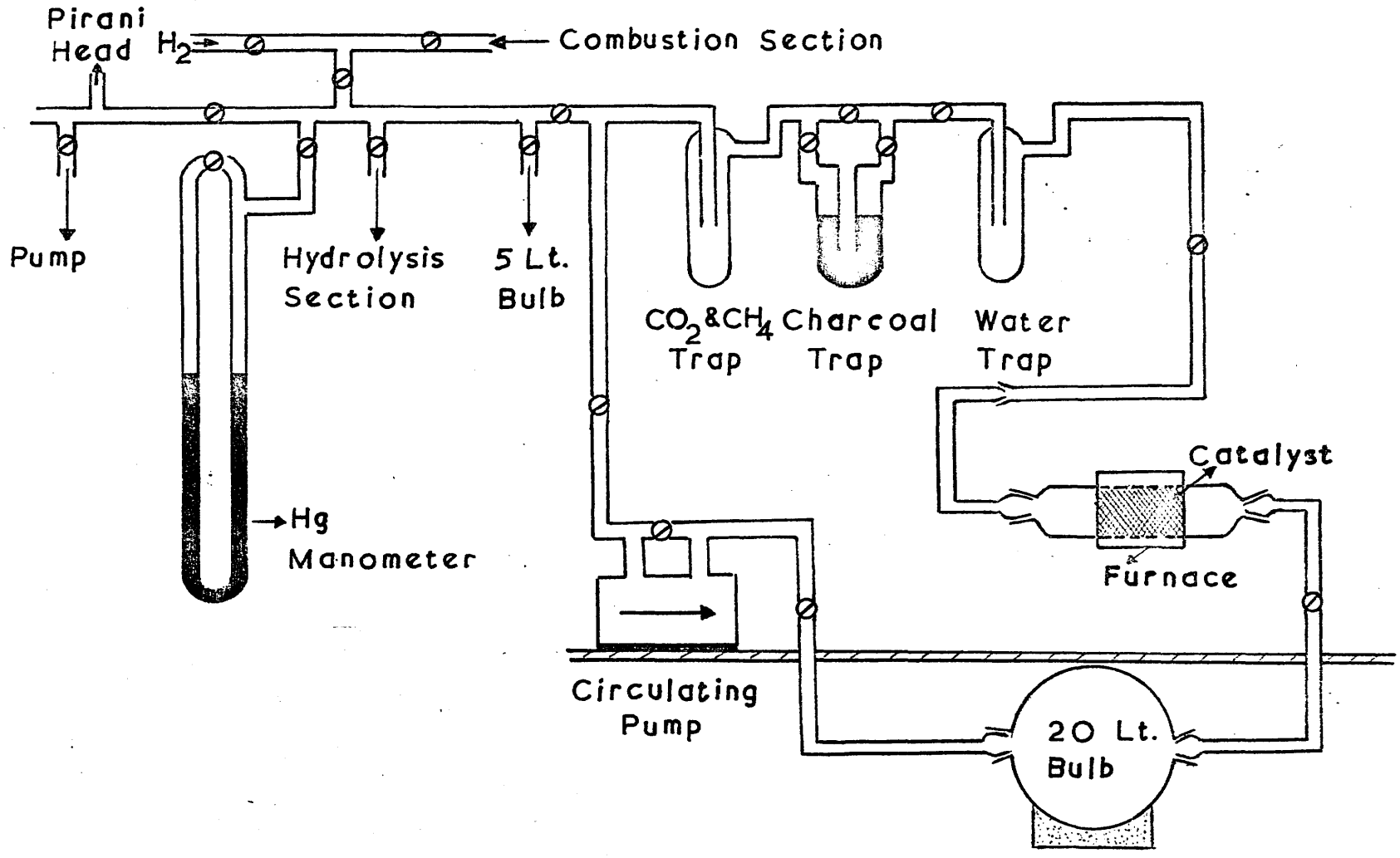
Sample g. oxalic acid	Amount of CO_2 1-atm expected	obtained	Yield %
14.08	5.11	5.01	99.7
14.16	5.12	5.03	98.2
13.38	4.76	4.67	98.1
14.82	5.27	5.14	97.5
14.61	5.19	5.15	99.2
13.31	4.73	4.70	99.4
13.86	4.93	4.89	99.2
		Average	98.8

2.1.3. Conversion of CO_2 to CH_4

The system employed has already been mentioned briefly but is described in more detail here.

Due to its very large volume (~23 l) the whole system (Figure 2.4) is evacuated in stages to a pressure of < 1 micron as registered on the Pirani gauge. The catalyst is heated to 350°C by an electric furnace controlled by a variable transformer. The purified CO_2 is transferred from the calibrated 5 l bulb to the first trap where it is condensed. At this point all stopcocks in the circulation section are opened except the four on either side of the catalyst and the charcoal trap. The stopcock preceeding the 5 l bulb is closed and the calculated amount of H_2 with 5% excess is admitted to the system from a gas cylinder. The gas pressure in the system is held at slightly less than 1 atm. at this stage. If the amount of H_2 required for the reaction would raise the total pressure in the system over 1 atm. it is introduced in two parts. After the H_2 is added the CO_2 is expanded into the system as quickly as possible. Warming the cold trap with a hairdrier helps to speed the expansion. The final pressure in the system is recorded, the stopcocks on both sides of the catalyst are opened, the circulation pump bypass is closed and the diaphragm pump switched on. In about 10 seconds the pressure begins to drop and water vapour droplets start to condense in the water trap, which is cooled by dry-ice, indicating that reaction has commenced. 30-40 min. is usually required to complete the reaction from the last addition of H_2. The reaction is considered complete when

Figure 2.4. CH_4 Synthesiser



the tubing connecting the furnace to the water trap is completely dry and the manometer mercury level remains constant. At this stage, the total pressure should be equal to the original CO_2 pressure plus the excess H_2 pressure, but in practice, the pressure on the manometer is always slightly less than this, probably because of the adsorption of small quantities of H_2 on the catalyst. When the reaction is considered complete the charcoal trap cooled with liquid nitrogen is introduced to the system and the charcoal trap bypass is closed. During the next 10 min., the CH_4 and H_2 are left to absorb on the charcoal. The circulation pump is then switched off, the bypass opened, and the system allowed to stand for a further 10 min. (A charcoal adsorption trap is necessary for the quantitative recovery of CH_4 due to its high vapour pressure, 11mmHg, at $-196^{\circ}C$). At the end of this time the system is slowly pumped off through the charcoal trap to ensure that all the CH_4 is absorbed. The stopcocks prior to the circulation pump and after the water trap are closed and the charcoal trap is pumped via the main pumping line to a residual pressure less than 200 micron. This removes traces of hydrogen from the gas. The trap (which was used to freeze out the CO_2 at the beginning) is cooled with liquid nitrogen and the stopcock before the circulation section is closed. The liquid nitrogen container surrounding the charcoal trap is removed and the charcoal is heated to room temperature to release the CH_4. When all the CH_4 is transferred to the CH_4 trap, the stopcocks above the charcoal trap are closed and the CH_4 trap can be pumped off for one or two seconds to ensure that

no H_2 is left, and then the CH_4 is expanded into the calibrated 5 l bulb to note the efficiency of the conversion. From here the CH_4 is transferred either to a storage bulb or to the counter through a trap cooled with dry-ice to condense any water vapour which may still remain in the gas.

Table 2.5 shows the results of efficiency experiments performed on the CH_4 synthesis - the average yield for ten successive experiments being about 95%.

An important feature of this procedure is that the catalyst and charcoal must be outgassed thoroughly to < 1 micron at temperatures 350°C and 200°C respectively before each synthesis to remove any residual gases.

2.1.4. Gas storage facilities and counter filling system

It is necessary to store gases prior to counting (to allow the decay of any radon impurity) and during counting sequences. The storage facility consists of ten 5 l glass bulbs (Figure 2.5), and usually 14 days storage is sufficient to allow the decay of any radon impurity. A mercury manometer attached to this section of the system allows the measurement of the gas volume in any bulb.

The counter filling system is constructed entirely from metal (Figure 2.6), and consists of a pressure gauge ranging from 0 to 200 psi; a stainless steel trap, 100ml in capacity; and 3 needle valves. The CH_4 counting gas is condensed into the stainless steel trap and the valve on the glass side closed. The valve on the detector side is opened to expand the gas into the counter at pressures up to 10 atm., the final pressure being recorded on

Table 2.5. Efficiency of CH_4 synthesis

CO_2 1-atm.	Obtained CH_4 1-atm.	Yield %
5.05	4.81	95.2
5.68	5.47	96.3
4.61	4.21	91.3
5.97	5.59	93.6
5.90	5.63	95.4
5.73	5.28	92.1
6.26	6.11	97.6
6.24	5.95	95.4
6.11	5.81	95.1
6.02	5.82	96.7
	Average	94.9

Figure 2.5. Storage Section

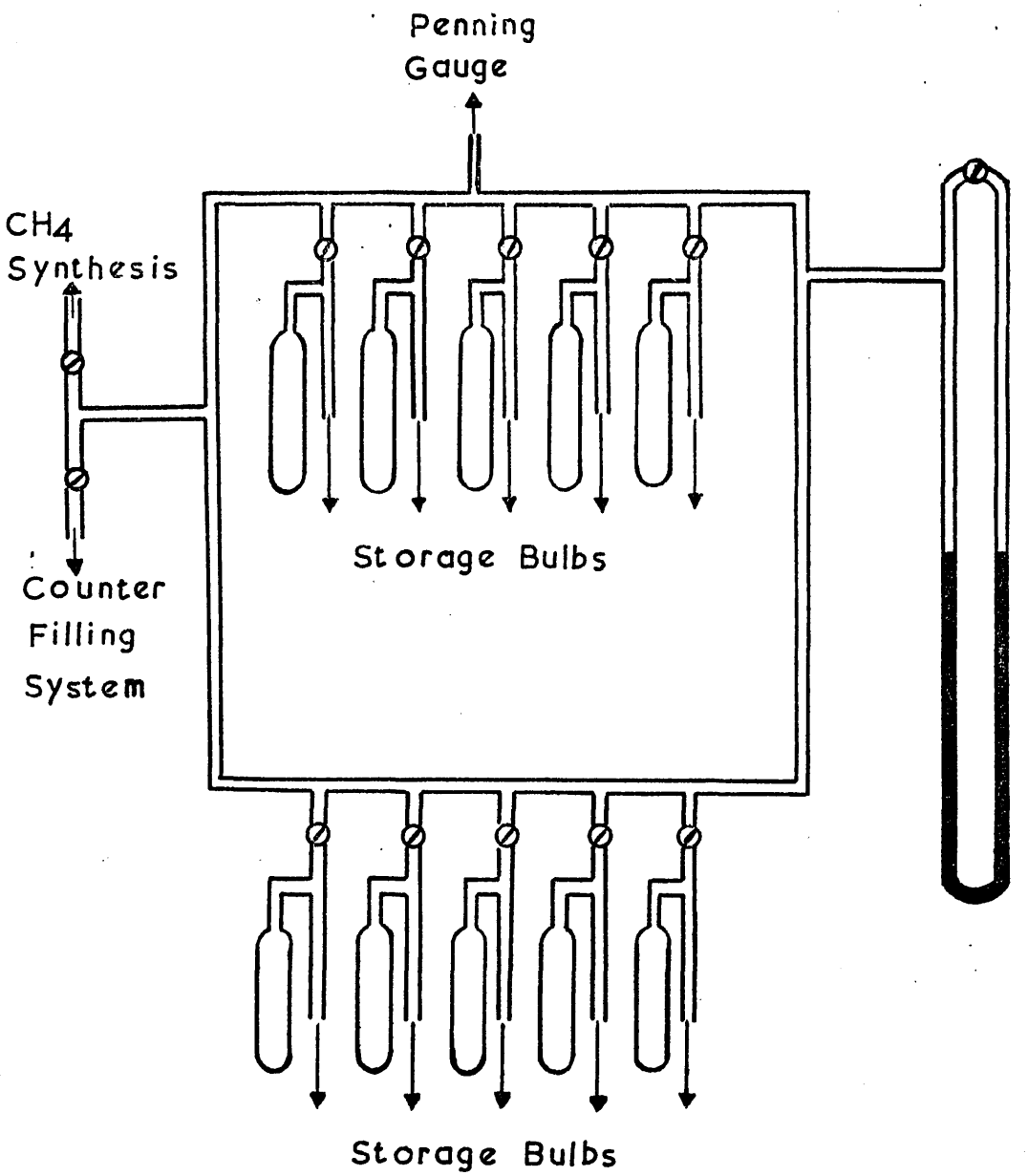
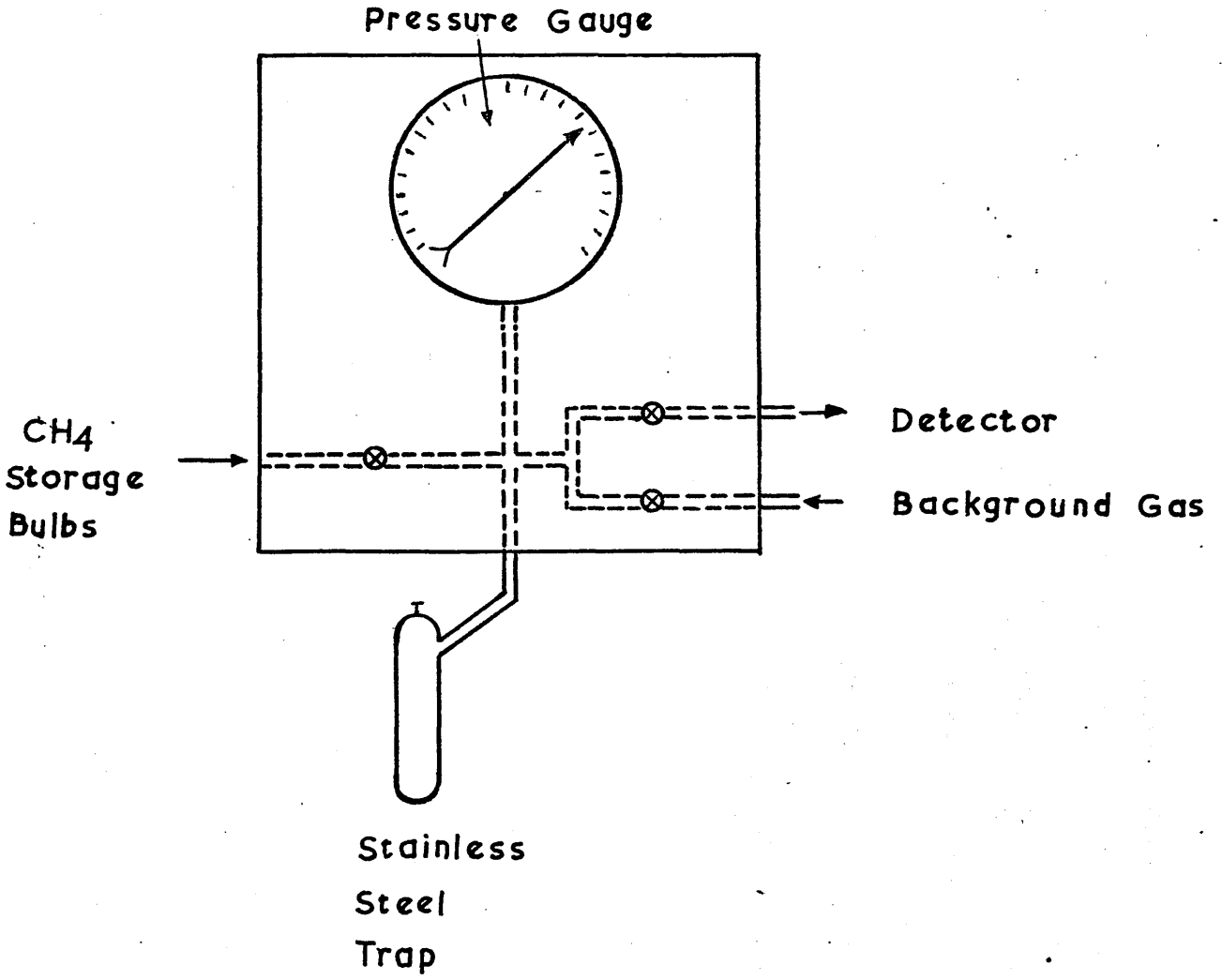


Figure 2.6. Counter Filling Section



the guage. The second valve on the right hand side allows standard background gas, stored in a high pressure cylinder, to be introduced directly into the system.

2.2. Gas Proportional Counting System for $^{14}CH_4$ Assay

Activity measurements are performed in a gas proportional counting system (Beckman Instruments Ltd., Glenrothes). The design of the system has been explained by Sharp and Ellis (1965), and it consists of two 0.5 l detectors surrounded by an anticoincidence guard counter, main and satellite electronics units, two data printers, and a three channel high voltage power supply. A block diagram of the system is shown in Figure 2.7.

2.2.1. Detectors, guard and shielding assembly

All detector cathode walls are constructed from oxygen-free high conductivity (O.F.H.C.) copper, with a thickness of ~1.8cm, to minimize the beta and gamma contribution to background, and are nickel-plated to absorb alpha activity contained in the copper. The detectors are designed to be filled at pressures up to 10 atm. and each contains an anode wire-diameter 0.0014 inch (Figure 2.8).

Surrounding the detectors is an anticoincidence guard counter constructed from two concentric copper cylinders (~2.5cm combined thickness) with a series of wire anodes mounted in the annular space. The guard counter is also operated as a proportional counter and is filled to a pressure of 80cm with CH_4. Once filled and sealed, this detector normally needs to be pumped out

Figure 2. 7. Block Diagram of Counting System

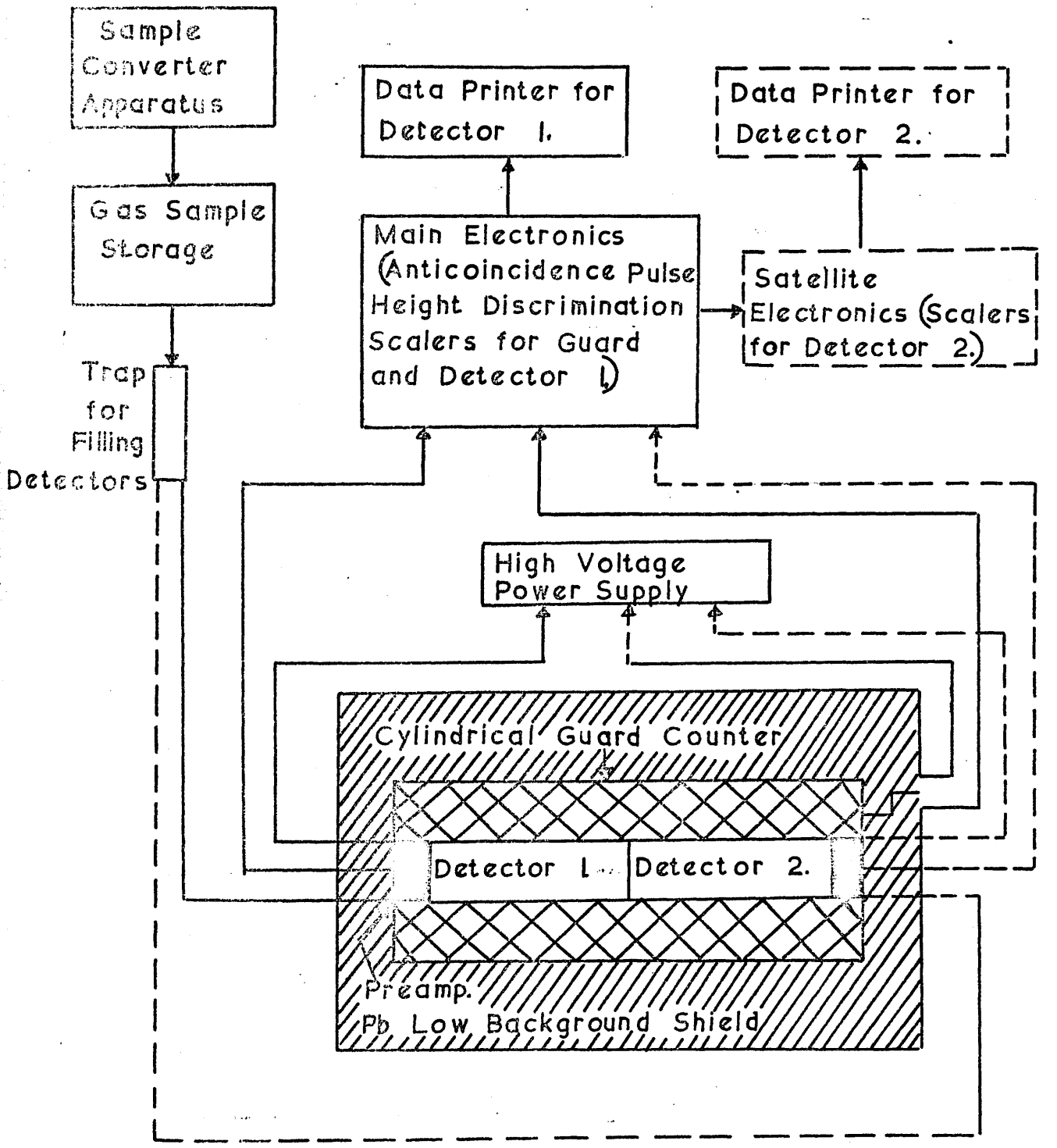
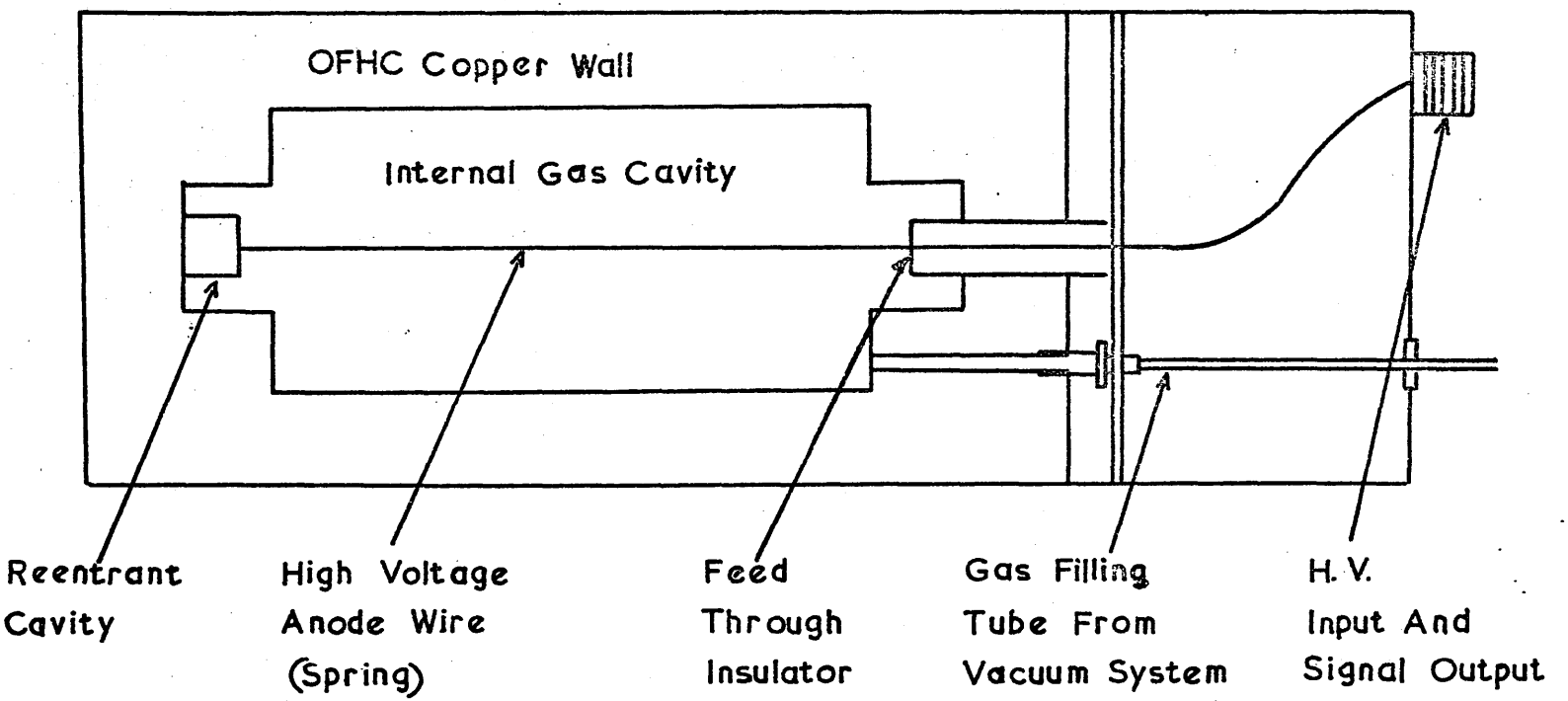


Figure 2.8. Cross Section Diagram Of Detector



and refilled only twice a year.

Each detector and guard counter has a separate preamplifier unit, and pulses registered in the detectors are fed via the preamplifiers to the main electronics unit.

The whole counting assembly is encased in a 4" thick lead shield (J. Girdler Co. Ltd., London) which measures 28" x 8" x 8" internally and 36" x 16" x 16" externally. A steel table is used to mount the shield which weighs approximately 3300 lb. Lead doors, encased in a steel frame, are provided at each end of the cabinet and are mounted on a vertical spindle and thrust bearing (Figure 2.9).

2.2.2. Main electronics, power supply and printers

Figure 2.10 shows a block diagram of the main electronics unit designed to operate with two detectors inside a single guard counter. Seven data outputs are provided from the main electronics console; detector gross unguarded rate, detector net low background beta rate, detector net low background alpha rate, for two detectors, and the guard count rate. There are three scalers in the main electronics unit, each of which can be switched to any of the seven outputs. Each scaler has its own timer. A satellite electronics unit provides an additional two scalers thus allowing the monitoring of any five of the seven outputs. A built-in test programme allows quick check-out of all circuitry.

The high voltage power supply consists of three channels, each of which is adjustable between 1000 and 10,000 volts using

Figure 2.9. Lead Shielding Assembly

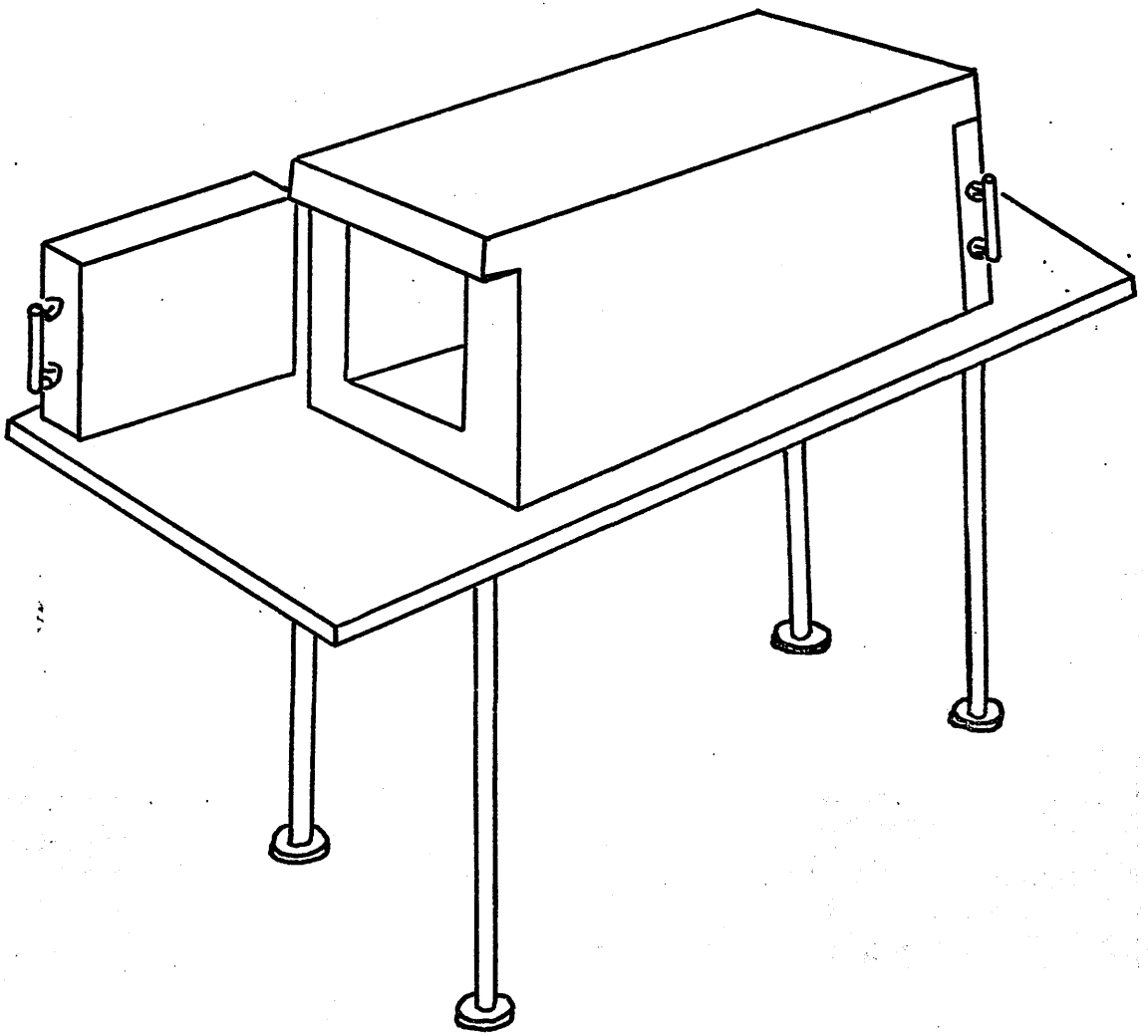
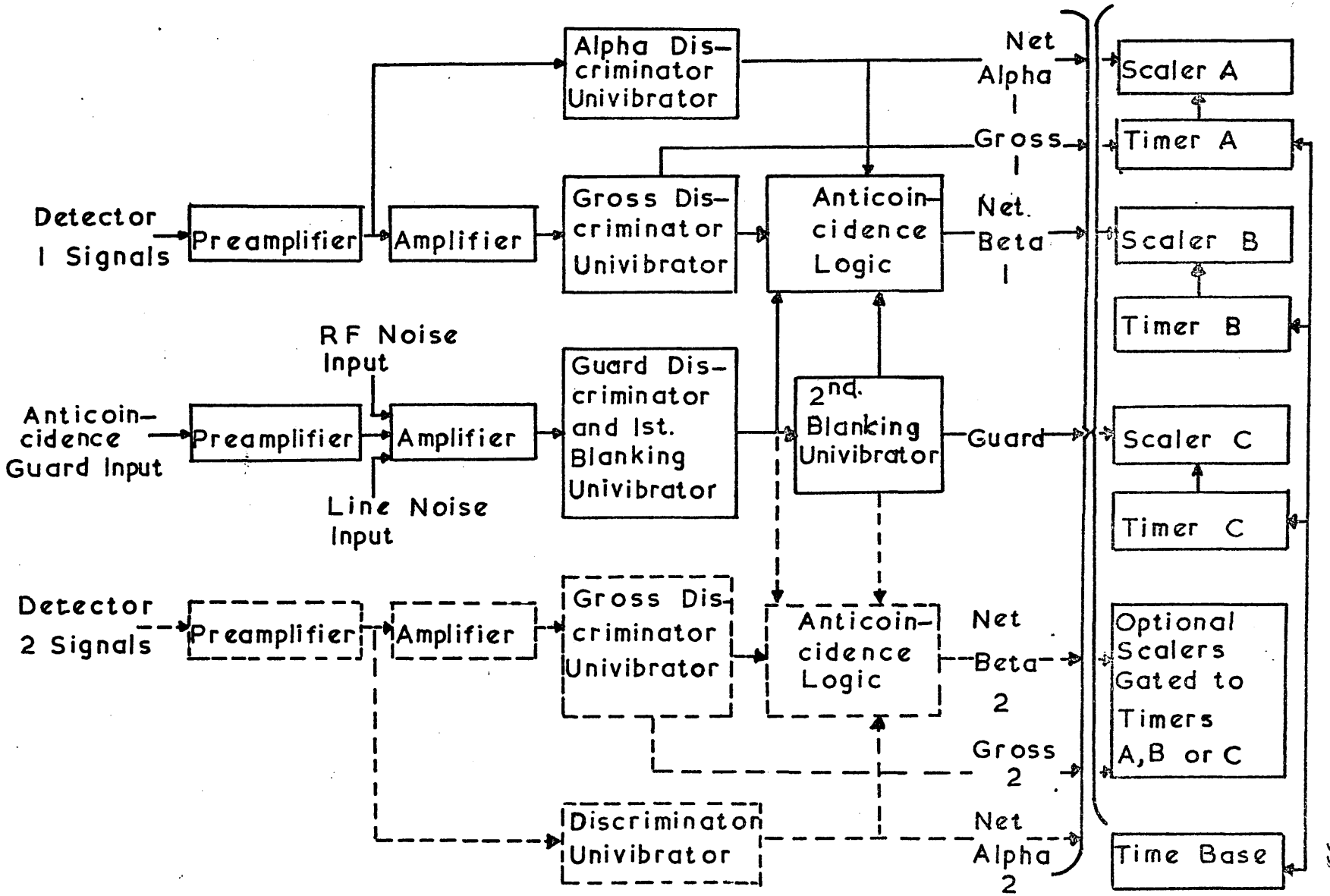


Figure 2.10. Main Electronics Block Diagram



helical potentiometers. Both detectors and the guard counter are fed by this unit.

Dual data printers provide automatically printed readouts for any two counting channels of the main electronics unit. The data printer utilizes two Sodeco printers and Sodeco preset timer, which permits a single long count to be subdivided into many shorter counting intervals (selectable from 0.1 to 999.9 min.). This enables examination of the data for statistical reproducibility, noise or drift, and the salvaging of "good" data even when a power failure may have occurred during a lengthy counting period. When a single detector only is being employed the two channel data printer normally monitors the detector gross unguarded rate and the detector net low background beta rate. Monitoring the gross unguarded rate provides a sensitive stability and reproducibility check on the detector using cosmic rays as the standard source.

2.2.3. Plateaux and background measurements

The plateau, operating voltage, and background count rate were determined for filling pressures from 1 atm. to 10 atm. In each case an excellent plateau at least 1000 volts in length and a slope of less than 0.5% per 100 volts was observed. As an example the plateau obtained for a routine filling pressure of 5 atm. is shown in Figure 2.11. The working voltage and background count rate as a function of filling pressure are shown in Figure 2.12 and Figure 2.13 respectively.

Figure 2.11. Detector Operational Characteristics

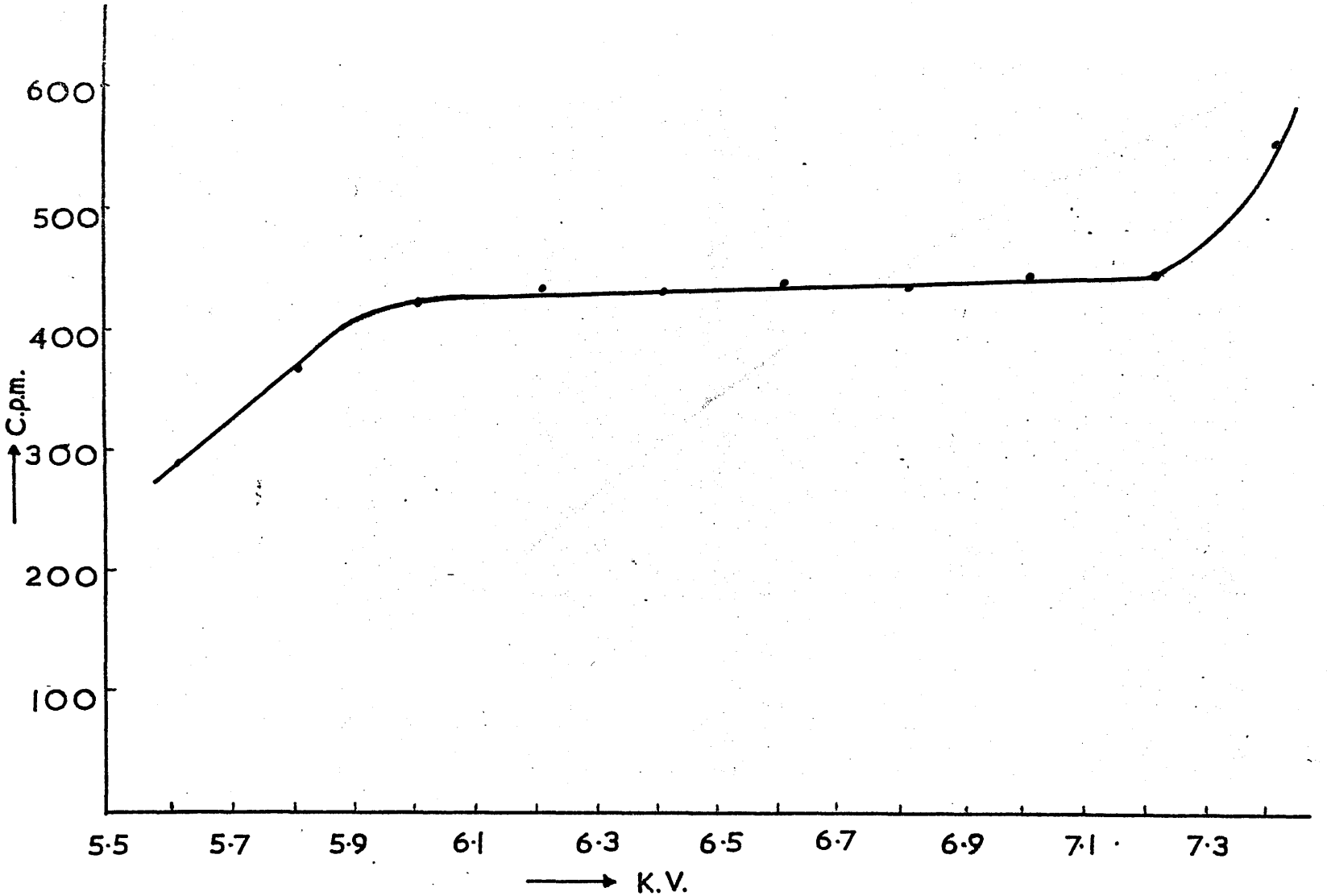


Figure 2.12. Operating Voltage as a Function of Filling Pressure

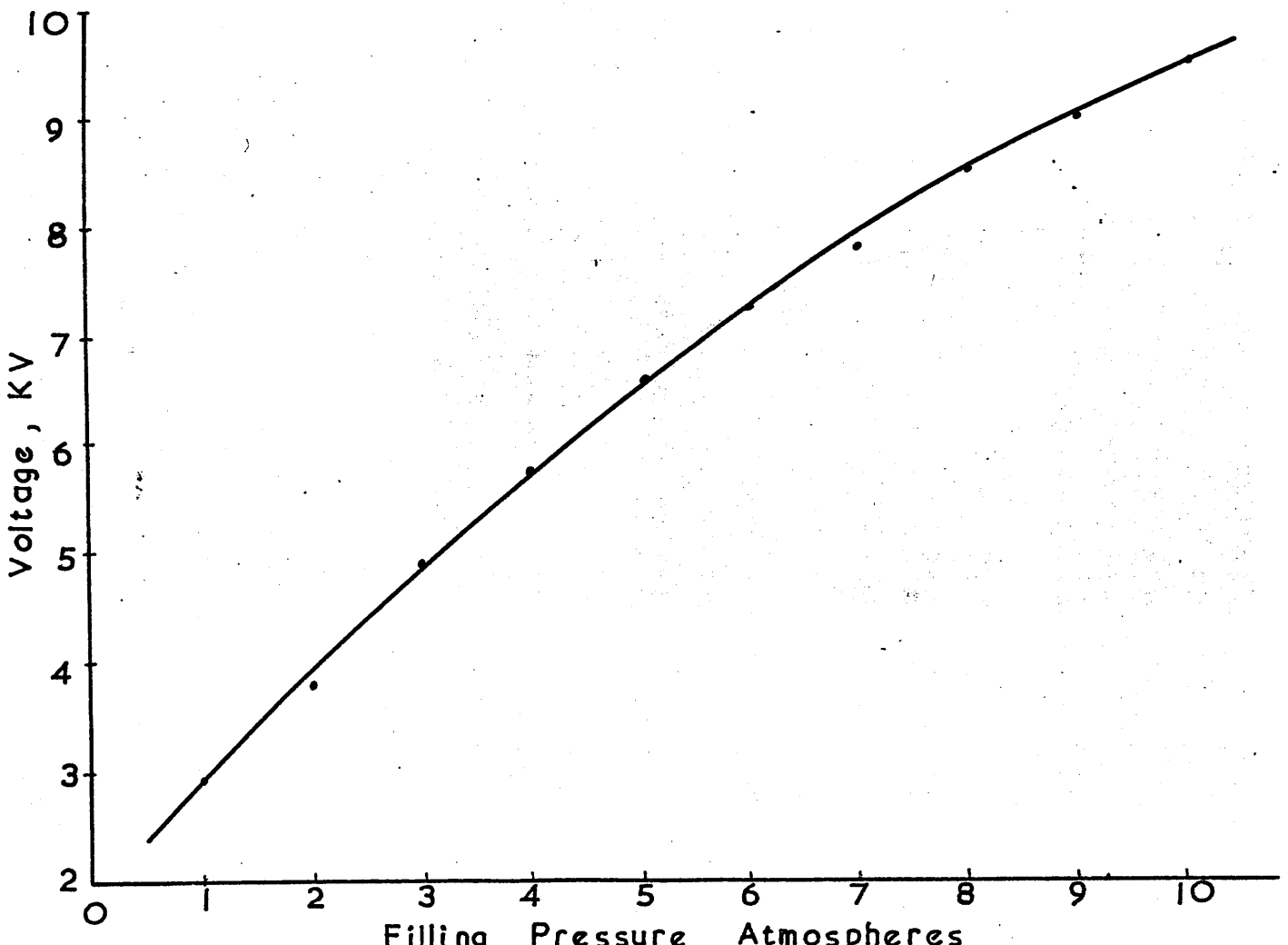
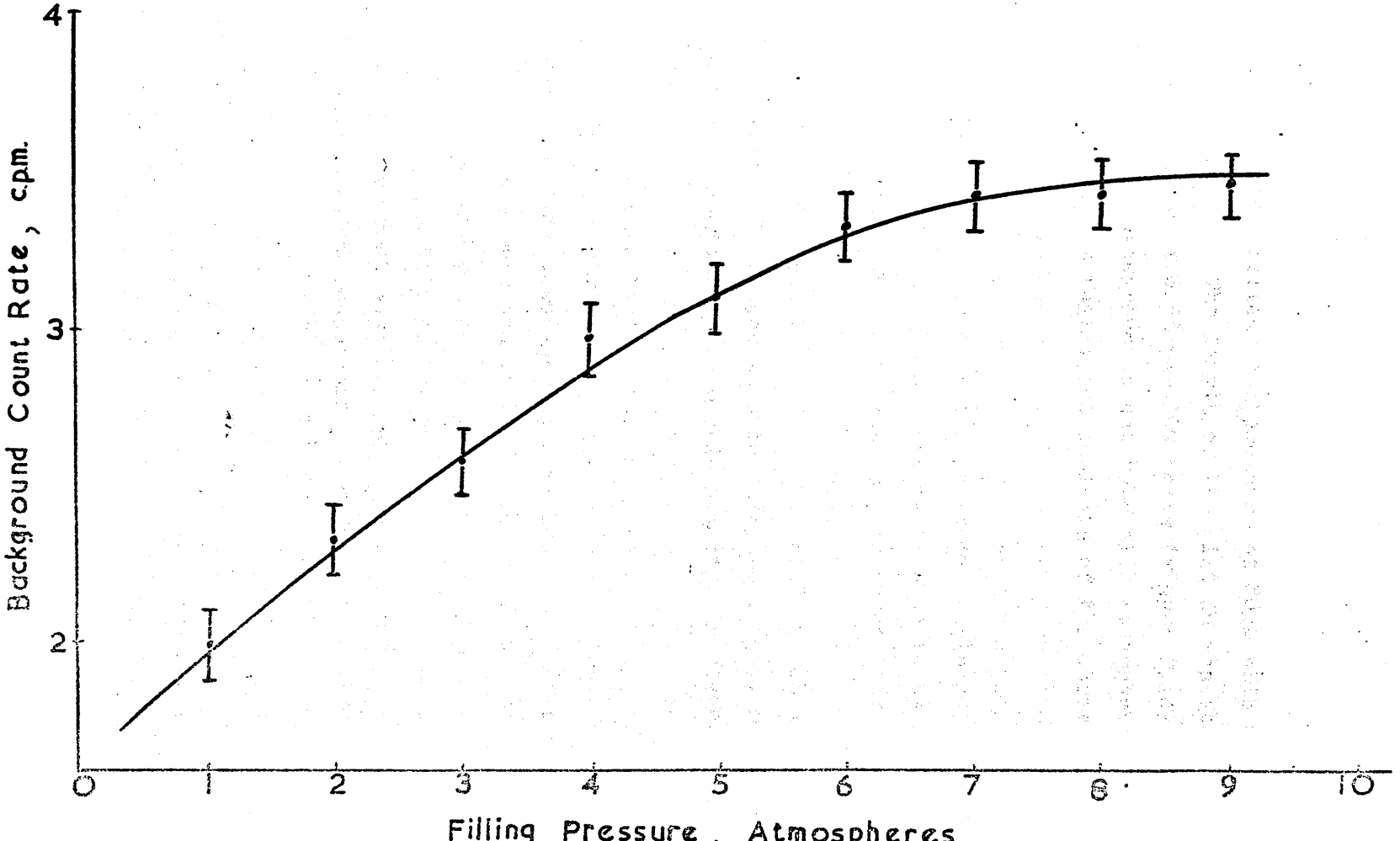


Figure 2.13. Variation of Background Count Rate as a Function of Filling Pressure



The guard counter, filled to a pressure of 80cm with CH_4, was similarly examined. The length of the plateau was about 800 volts with a slope of 0.5% per 100 volts (Figure 2.14).

The variation of background count rate with atmospheric pressure was studied. A regression analysis of the observations for the first year of operation indicated a variation of -0.11 counts/cm Hg at a filling pressure of 5 atm. as shown in Figure 2.15, (See Appendix A for the computer programme employed). Observations made during the second year were found to be in excellent agreement with the first year's data suggesting that long-term drift of electronic performance is small.

Sources for the preparation of non-active CH_4 which would be used for background purposes were investigated, viz., marble (obtained from I.A.E.A.'s radiocarbon laboratory, in Vienna), and anthracite. A third source of background gas is "tank" CH_4, (supplied by Beckman Instruments Inc., California) reputed to have been manufactured from petroleum sources. Two sources of H_2, (Air Products Ltd., and Messer Griesheim GmbH) believed to be non-radioactive, were available for the reduction of CO_2 to CH_4. The background gas produced from marble with Air Products' H_2 gave a slightly higher count rate than the "tank" CH_4. The same experiment was then repeated with the H_2 supplied by Messer Griesheim GmbH, Dusseldorf. No difference was observed on this occasion between the CH_4 derived from marble and the "tank" CH_4. The difference between these results was attributed to the contamination of H_2 by tritium (see Long, 1965). Table 2.6 compares the CH_4 activity data obtained from syntheses using

Figure 2.14. Guard Counter Operational Characteristics

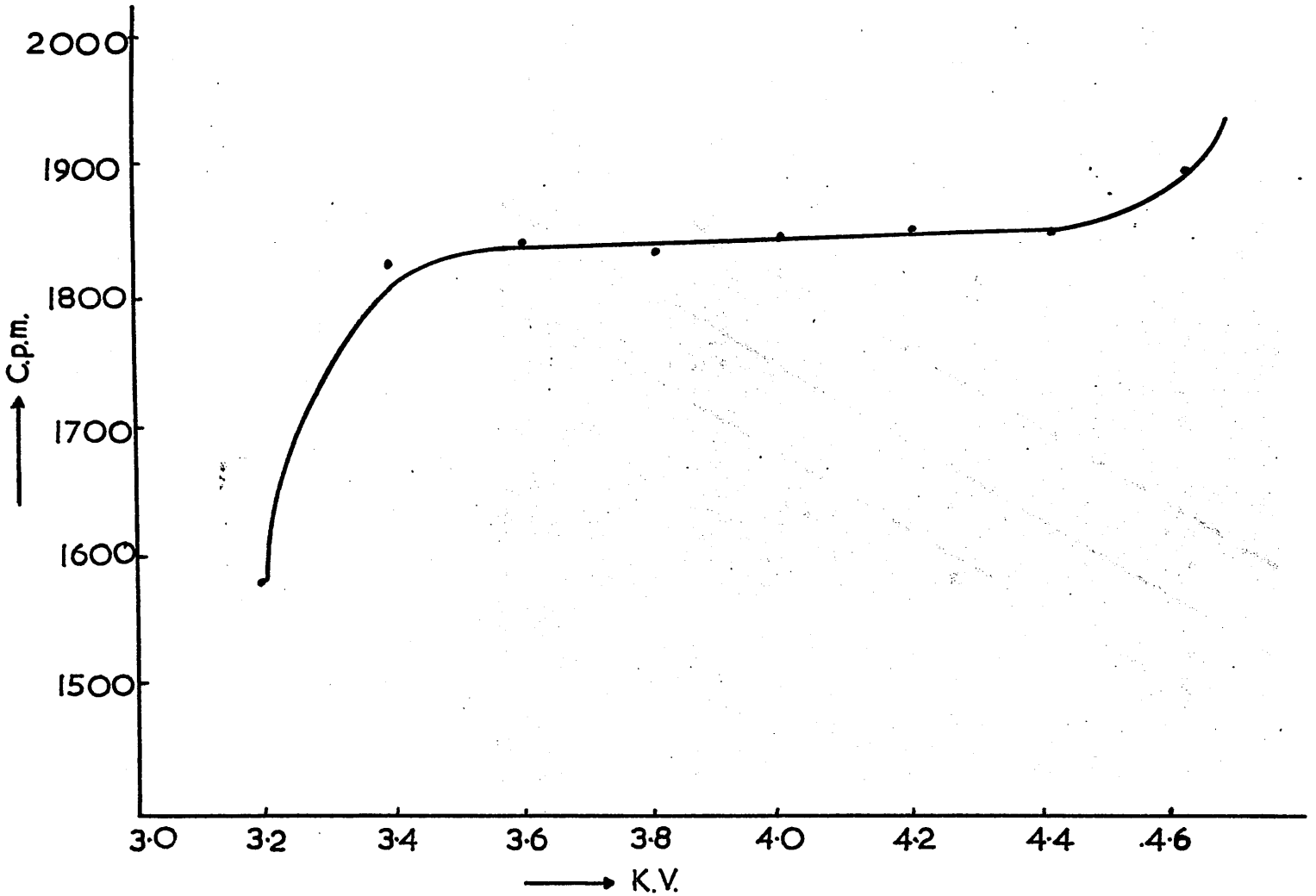


Figure 2.15. Variation of Background as a Function of Barometric Pressure

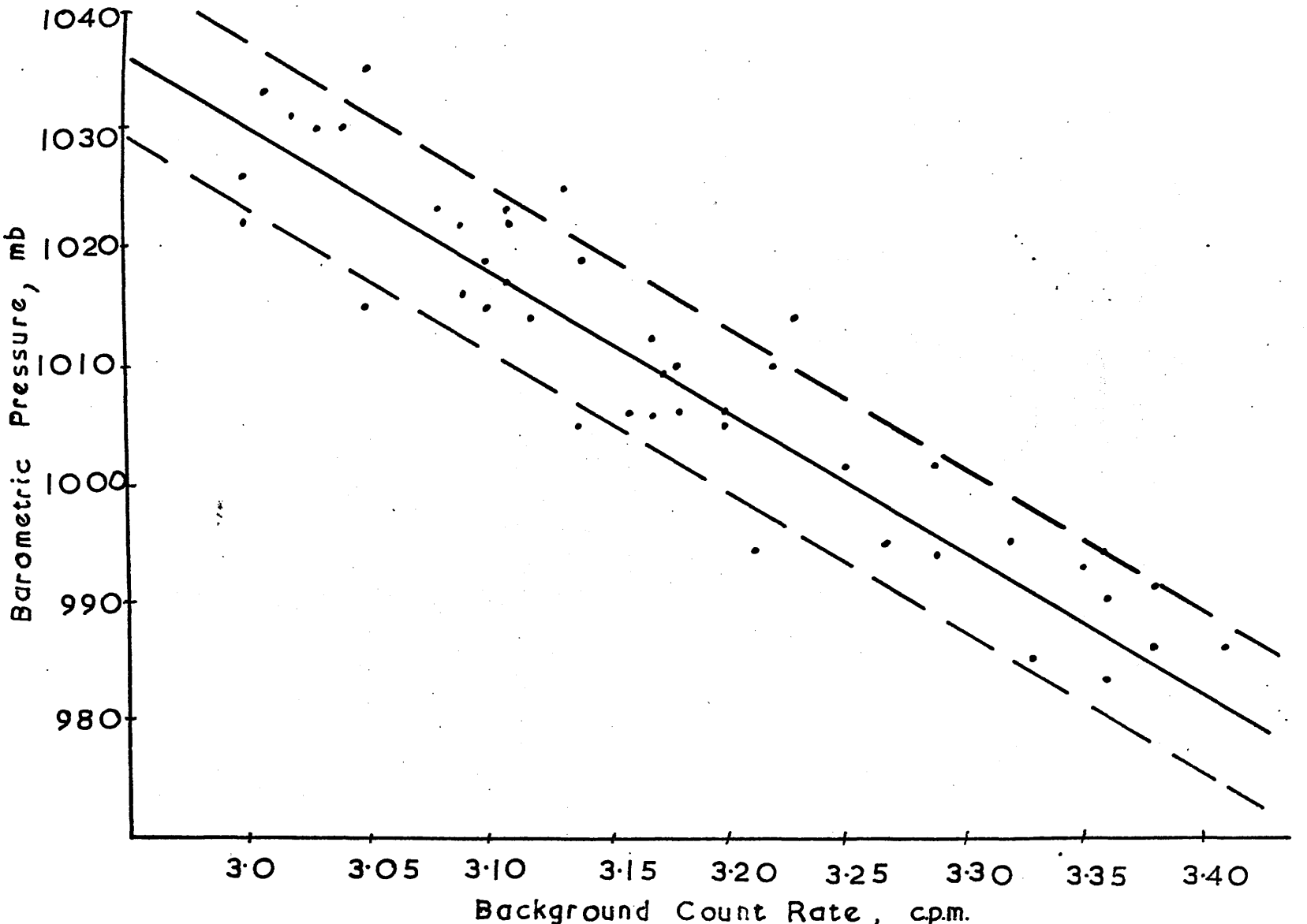


Table 2.6. Measurement of possible tritium contamination in Messer Griesheim hydrogen.

Mess.Gries.' hydrogen cpm ± 2σ	"Tank" Methane cpm ± 2σ	"Tritium"
3.19 ± 0.07	3.18 ± 0.06	0.01 ± 0.09
3.29 ± 0.10	3.29 ± 0.06	0.00 ± 0.12
3.18 ± 0.09	3.14 ± 0.06	0.04 ± 0.11
3.09 ± 0.07	3.06 ± 0.06	0.03 ± 0.09
3.23 ± 0.06	3.14 ± 0.06	0.09 ± 0.08
3.11 ± 0.09	3.11 ± 0.06	0.00 ± 0.11
3.03 ± 0.07	3.01 ± 0.06	0.02 ± 0.09
	Average	0.03 ± 0.04

Messer Griesheim' H_2 and the "tank" CH_4, and Table 2.7 compares the activity data obtained on "tank" CH_4 and CH_4 synthesised from Air Products' H_2. The recorded contamination in CH_4 synthesised from Air Products' H_2 is about 0.13 ± 0.04 cpm for a filling pressure of 5 atm. No radon contamination was observed in any background gas.

Since the "tank" CH_4 appears to have no radioactive contamination, it has been used as background gas throughout this research. The background count rate at sea level is 3.13 ± 0.10 (2σ) cpm at 1 atm. barometric and 5 atm. filling pressures. This residual background is the sum of the following components:

(a) Ionizing particles not detected by the anticoincidence arrangement.

(b) α and β contamination of the counter wall,

(c) Compton-, photo-, and pair-electrons produced by radiation in the counter wall and in the gas. The source for γ rays can be either radiocative contaminants in the shield or γ rays associated with the cosmic-ray flux passing through the shield.

By choosing a concentric-wall multiple anode guard the contribution from the first component to the background is reduced to a minimum value. The construction material (O.F.H.C. copper) of the counter combined with the nickel surface coating minimize the β, γ and α contribution. The small internal volume (0.5 l), consequently the small cathode area of the detector also helps to reduce background considerably.

Table 2.7. Measurement of possible tritium contamination in Air Products' hydrogen.

CH_4 made with Air Products' hydrogen cpm ± 2σ	"Tank Methane" cpm ± 2σ	"Tritium"
3.19 ± 0.07	3.06 ± 0.06	0.13 ± 0.09
3.23 ± 0.06	3.11 ± 0.06	0.12 ± 0.08
3.59 ± 0.11	3.42 ± 0.06	0.17 ± 0.13
3.27 ± 0.07	3.13 ± 0.06	0.14 ± 0.09
3.27 ± 0.07	3.11 ± 0.06	0.16 ± 0.09
3.19 ± 0.09	3.09 ± 0.06	0.10 ± 0.11
3.16 ± 0.07	3.05 ± 0.06	0.11 ± 0.09
3.09 ± 0.06	3.00 ± 0.06	0.09 ± 0.08
3.47 ± 0.06	3.32 ± 0.06	0.15 ± 0.08
	Average	0.13 ± 0.04

2.2.4. Modern standard activity and sample counting

Standard CH_4 gas is prepared from the N.B.S. (National Bureau of Standards) oxalic acid standard. The activity of this gas is measured fortnightly and the net value for each determination calculated by subtraction of the appropriate background count and correction for filling temperature. The mean net value is calculated for all determinations agreeing within 2σ error. Further corrections are applied to this value to allow for both the radioactive decay since preparation of oxalic acid and any isotopic fractionation during CO_2 preparation. The average value obtained from measurements over a period of 16 months is 18.76 ± 0.12 (2σ) cpm at 5 atm. filling pressure at 18°C (Table 2.8).

Samples are counted at least twice, several days apart, for a minimum of 30,000 counts (~17 hours) at the first count and 10,000 counts (~ 6 hours) on the second occasion. The mean barometric pressure is noted for each counting period and the average net count rate is calculated for all determinations agreeing within the 2σ error.

2.3. Data Processing and Calibration Studies

2.3.1. Mass spectrometry and calculation of carbon-14 enrichment values.

Mass spectrometric measurements are necessary to correct the carbon-14 counting rates for any fractionation (with respect to a standard) of the carbon isotopes that may have taken place

Table 2.8. Variation of specific activity of oxalic acid standard with time (cpm ± 2σ).

Date of counting	Standard I*	Standard II	Standard III
9.12.67	18.22 ± 0.30		
27.12.67	18.12 ± 0.27		
7. 1.68	17.92 ± 0.30		
23. 1.68	18.27 ± 0.37		
12. 2.68	18.07 ± 0.27		
14. 3.68	18.28 ± 0.27		
1. 4.68	18.31 ± 0.29		
4. 5.68		18.87 ± 0.25	
24. 5.68		18.74 ± 0.25	
5. 6.68		18.43 ± 0.27	
17. 6.68		18.63 ± 0.27	
24. 6.68		18.57 ± 0.29	
1. 7.68		18.81 ± 0.27	
4. 7.68		18.30 ± 0.30	
26. 7.68			18.58 ± 0.27
7. 8.68			18.32 ± 0.29
19. 8.68			18.33 ± 0.28
3. 9.68			18.43 ± 0.29
19. 9.68			18.52 ± 0.29
11.10.68			18.25 ± 0.26
29.10.68			18.51 ± 0.25
13.11.68			18.70 ± 0.29
30.12.68			18.37 ± 0.26
14. 1.69			18.63 ± 0.27
6. 2.69			18.75 ± 0.30
25. 2.69			18.67 ± 0.28
20. 3.69			18.82 ± 0.29
13. 4.69			18.68 ± 0.27

* Mass spectrometric measurement on this standard was not available; a value of -19‰ was assumed.

in nature or during the collection and preparation of the counting gas. Samples of CO_2 gas are taken for the measurement of the $^{13}C/^{12}C$ ratio.

Craig (1953) has discussed the relationship between the $^{13}C/^{12}C$ ratio in natural systems and shown that the enrichment of Carbon-14 in a given compound should be almost exactly twice that of the carbon-13 enrichment.

The $^{13}C/^{12}C$ ratio results are expressed with respect to a standard using the relationship:

$$\delta^{13}C = \left(\frac{^{13}C/^{12}C \text{ sample} - ^{13}C/^{12}C \text{ standard}}{^{13}C/^{12}C \text{ standard}} \right) \times 1000 \text{ ‰}$$

19th century wood was used initially as the standard, and the $\delta^{13}C$ value for CO_2 formed by the combustion of wood is usually -25‰ with respect to PDB Ch. Lst. Std. (Peedee Belemnite Chicago Limestone Standard).

Mass spectrometric analyses were performed at the National Physical Laboratory, Middlesex, with an MS 3 double beam collector system. For $\delta^{13}C$ measurement CO_2 from the sublimation of dry-ice was used as a secondary standard. The measured enrichment of this gas is -25‰ relative to PDB Ch. Lst. Std., i.e., it is equivalent to 19th century wood. Therefore the final result was calculated with the following formula:

$$\delta^{13}C \text{ sample} = (\delta^{13}C \text{ enrichment} - 25) \text{ ‰}$$

Carbon-14 values are quoted as per millage enrichment with

respect to 0.950 times the activity of the NBS oxalic acid which is regarded as equivalent to the activity of age corrected 19th century wood. It will be noted that results are expressed both in terms of $\delta^{14}C$ and Δ. The former term has little significance and refers to the enrichment measured prior to correction for isotopic fractionation occurring in the sample and/or its processing in the laboratory.

Calculations are carried out using the method described by Broecker and Olson (Radiocarbon, Vol. 3, p. 176-204, 1961).

$$\delta^{14}C = \left(\frac{\alpha A_s}{0.950 A_m} - 1 \right) \times 1000 \text{ ‰}$$

where, α = Dilution factor applied in cases where sample dilution with inactive material has occured, $\alpha \geq 1$.

A_s = The sample specific activity corrected for decay due to its age.

A_m = The specific activity of NBS oxalic acid.

$$\Delta = \delta^{14}C - (2\,\delta^{13}C + 50)\left(1 + \frac{\delta^{14}C}{1000}\right)$$

where $\delta^{13}C$ is the per mil difference between the ^{13}C content of the sample and the standard belemnite sample.

Reported ages are calculated using the following relationship:

$$\text{Age } (T) = 8033 \log_e \frac{1}{1 + \Delta \times 10^{-3}}$$

Calculations of the errors in $\delta^{14}C$ and Δ values, and ages are based on the procedure described by Callow et al (1965).

Craig (1961) has made a survey of mass spectrometric analyses of radiocarbon standards. He analysed 24 samples of CO_2 from the oxidation of NBS oxalic acid radiocarbon standard (submitted from 13 radiocarbon laboratories throughout the world) for ^{13}C content in order to provide comparative data for normalizing the counting results. Using his proposal the age-corrected NBS oxalic acid standard is normalized to a $\delta^{13}C$ value of -19‰ with respect to PDB Ch. Lst. Std.

N.B.S. oxalic acid is our laboratory standard and all carbon-14 measurements of oxalic acid are normalized for ^{13}C as follows:-

$$A_o = A \left[1 - \frac{2(\delta^{13}C \text{ std.} + 19)}{1000} \right]$$

where, A = The actual measured counting rate corrected for decay.

$\delta^{13}C$ std. = The $\delta^{13}C$ value of N.B.S. oxalic acid expressed with respect to PDB Ch. Lst. Std.

2.3.2. Results of intercalibration experiments

Before routine measurement of carbon-14 activities and ages began a number of samples were requested from various established laboratories for intercalibration purposes. The results of these samples, as shown in Table 2.9 proved the validity of our method of gas preparation and counting technique.

Table 2.9. Intercalibration of carbon-14 assays

Sample description	The age of sample in years			
	Glasgow Univ.	Birmingham Univ.	Lamont Geo.Obs.	T. Hamada, Japan, Inst. Phys. Chem.
Charcoal (Birch-Betula)	1908 ± 60		2100 ± 80	
Marine Shell (Arctica Islandica)	11,787 ± 122			11,900 ± 170
Peat (from Redkirk point)	11,828 ± 105	11,205 ± 177		

2.4. Possible Sources of Error

The measurement of the carbon-14 activity of a sample is subject to a considerable number of errors. The most common errors are (a) radioactive contamination, (b) contamination with carbonaceous material, (c) fractionation of the carbon isotopes, (d) variation in the filling of the counter, (e) spurious pulses due to electronic difficulties, (f) variation in the counting efficiency, (g) variation in the background, and (h) memory effects of the counter.

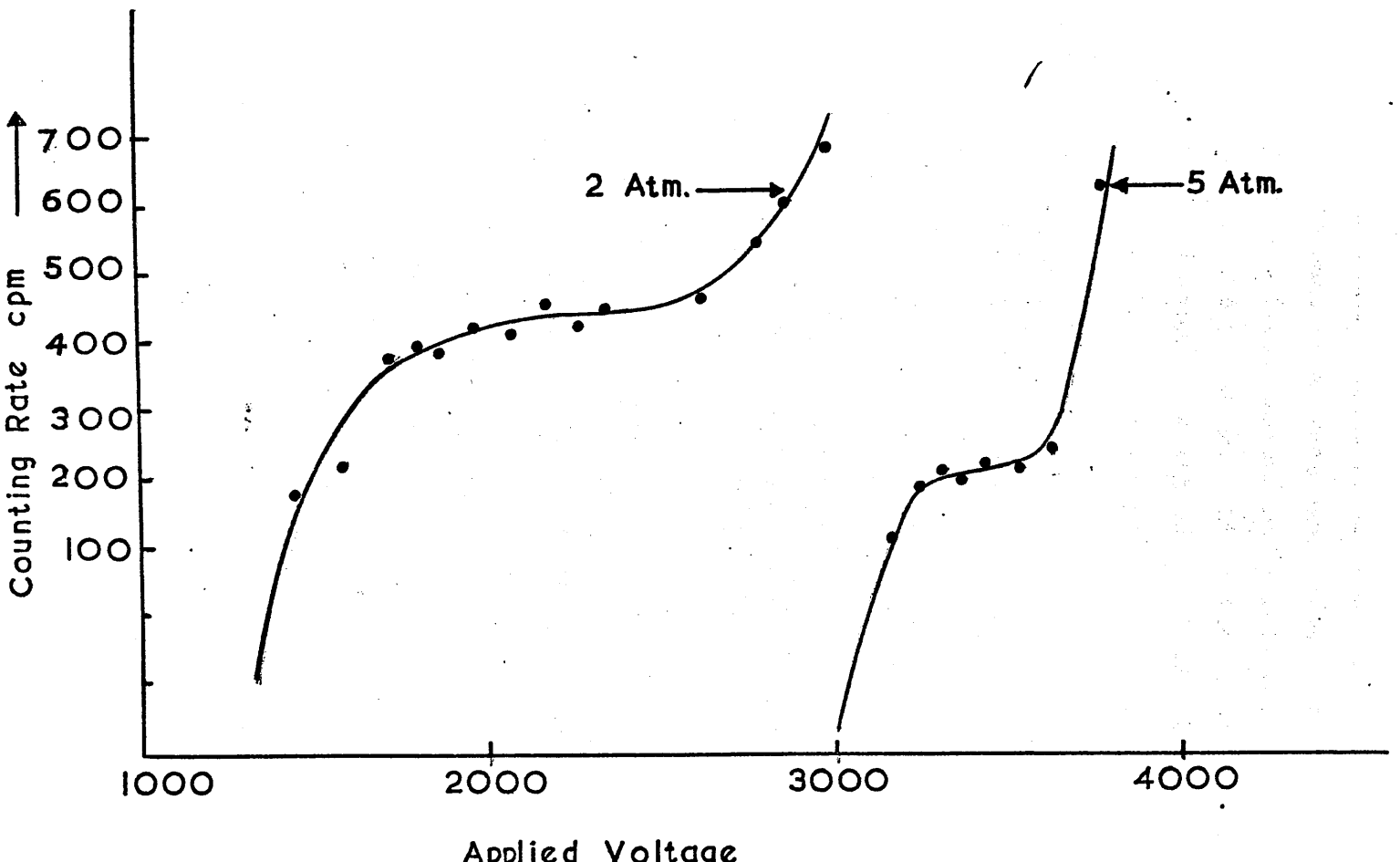
Radon contamination was observed in the early samples derived from atmospheric CO_2. The only possible source of this contamination was the $BaCl_2$ used to precipitate the $BaCO_3$ from solution. Three types of commercial $BaCl_2$ have been tested for radium content by measuring the radon present in the sample gas (Table 2.10). The radon contamination was least in the product manufactured by B.D.H. Chemicals Ltd. Although an α-plateau of the counter has been determined (Figure 2.16) the samples are generally stored for two weeks prior to counting to allow the decay of possible contamination of radon and its daughter products rather than direct measurement.

In the case of atmospheric CO_2 samples there are two possible sources for the contamination with carbonaceous material (1) The KOH solution may contain some carbonate, (2) CO_2 may be picked-up from the laboratory atmosphere during the $BaCO_3$ precipitation. The first possibility was eliminated

Table 2.10. Investigation of radon contamination from various sources.

Sample	Date of gas production	Dates of counting	Net activity cpm ± 2σ		Radon and its daughter products
Atmospheric CO_2 as $BaCO_3$ (1) (Hydrolysis)	14.12.1967	14/15.12.1967	40.58 ± 0.57		5.5 pc
		3. 1.1968	28.57 ± 0.37		
		9. 1.1968	27.94 ± 0.33	28.26 ± 0.20	
		18. 1.1968	28.27 ± 0.36		
Atmospheric CO_2 as $BaCO_3$ (1) (Hydrolysis)	19.12.1967	19/20.12.1967	37.15 ± 0.45		3.8 pc
		8. 1.1968	28.47 ± 0.33		
		17. 1.1968	29.05 ± 0.33	28.76 ± 0.23	
Atmospheric CO_2 as $BaCO_3$ (2) (Hydrolysis)	16.12.1967	16.12.1967	66.62 ± 0.71		17.0 pc
		4. 1.1968	28.88 ± 0.33		
		19. 1.1968	28.66 ± 0.28		
		24. 1.1968	28.88 ± 0.50	28.84 ± 0.22	
Atmospheric CO_2 as $BaCO_3$ (3) (Hydrolysis)	28.12.1967	28/29.12.1967	29.07 ± 0.35		negligible
		22. 1.1968	28.46 ± 0.32		
		31. 1.1968	28.53 ± 0.38		
Oxalic acid Standard (wet oxidation)	8.12.1967	9.12.1967	18.22 ± 0.30		None
		27.12.1967	18.12 ± 0.27		
		23. 1.1967	18.27 ± 0.37		
Charcoal (combustion)	20.12.1967	20/21.12.1967	13.68 ± 0.30		None
		28.12.1967	13.53 ± 0.26		

Figure 2.16. Detector Alpha Plateaux at Filling Pressures of 2Atm. and 5Atm.



by precipitating any carbonate present in the KOH solution as $BaCO_3$. As to the second, blank runs have shown that this effect was negligible, i.e., maximum $BaCO_3$ collected under experimental conditions was 0.2g. Since the normal yield from any exposed solution is in the range of 80 - 110g $BaCO_3$, the maximum contamination is therefore < 0.3% which is within the limitations of statistical counting error (1g $BaCO_3$ ≈ 0.1135 l CO_2 at S.T.P.).

In the treatment of organic, especially dating samples, particular attention was paid to avoid contamination of the samples with recent materials, i.e., paper and impregnating materials.

The high production efficiencies (95-100%) achieved have served to minimize the error due to fractionation of carbon isotopes during chemical preparation. Further, mass spectrometric measurements were made on every sample to correct for any fractionation that had taken place either in nature or in the laboratory.

The temperature of the gas during the filling is recorded and necessary pressure corrections made. In Figure 2.17 the correction factor as a function of filling temperature has been plotted. The factor was chosen to be 1.000 for 18°C arbitrarily.

In any sensitive electronic system there is always the possibility of recording extraneous counts due to pick-up of external electrical noise and high voltage breakdowns. In our system the automatic data printers allow us to make corrections as mentioned before, and also the inclusion of an RF antenna

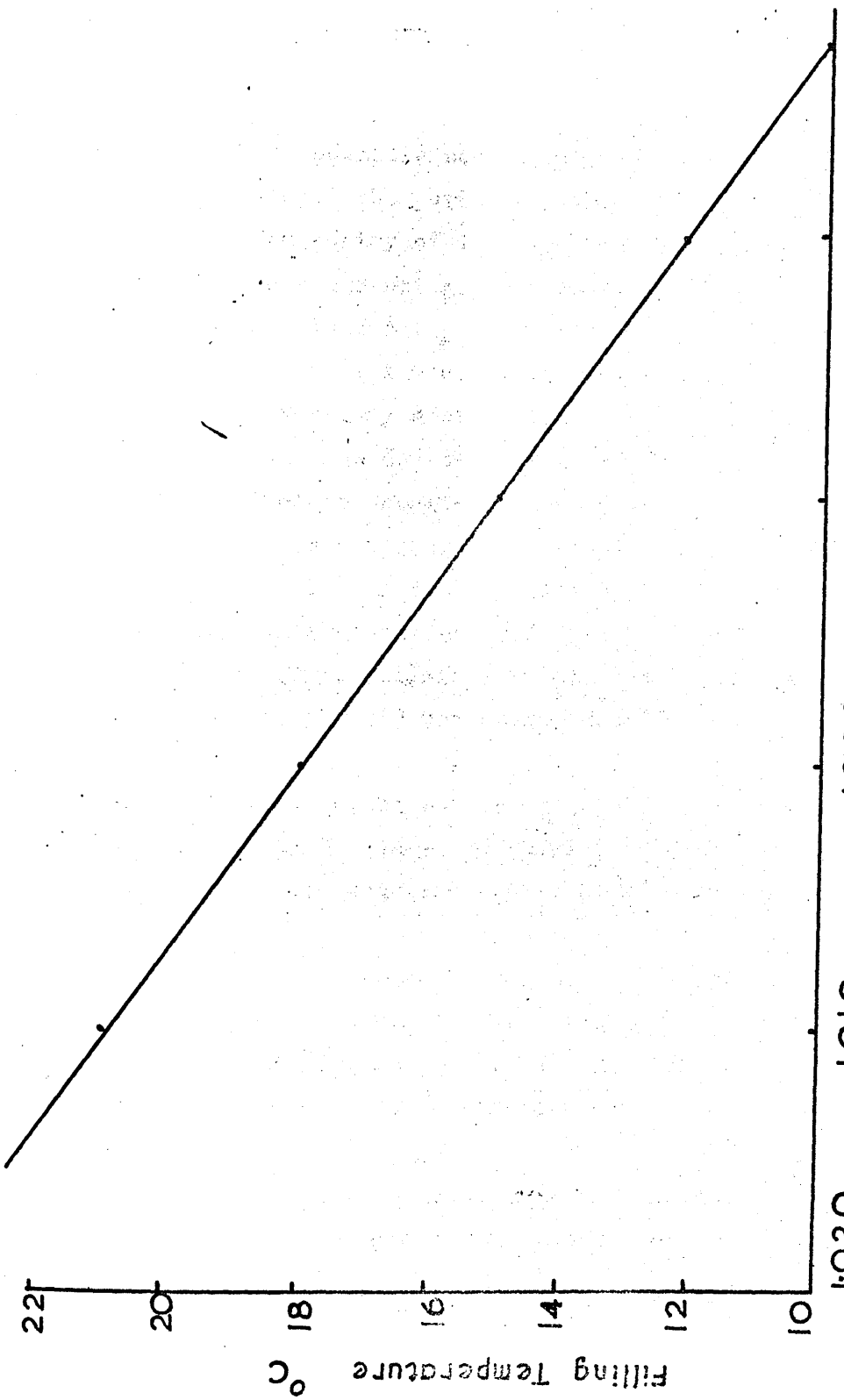


Figure 2.17. Pressure Correction Factors as a Function of Filling Temperature

cancels spurious pick-up in the console electronics.

There are two possible sources for variation in the counting efficiency; the purity of the gas, and the electronic sensitivity. The purity of the gas is monitored from the difference of gross and net β count rates as recorded by the printers. Gross minus net β (Δ) is the number of coincidence events and a measure of the cosmic ray flux which is essentially constant. Therefore any decrease in the Δ value will indicate the impurity of the gas due to loss of anticoincidence events by the action of electronegative impurities. Another indication for an impure gas is the length of the plateau. As the gas becomes impure the length of the plateau becomes shorter. Since the count rate of the standard gas has remained constant within the error ($\pm 2\sigma$) limits, we can assume that the electronic sensitivity did not change during the time of this study.

The variations in the background could be a serious source of error especially for very old samples. DeVries and Barendsen (1953) and Fergusson (1955) have shown that these variations are largely of natural origin due to fluctuations in the cosmic-ray flux at the surface of the earth. This has been demonstrated by correlating the background counting rate with atmospheric pressure. Since a large part of the cosmic ray flux is absorbed by the atmosphere the amount reaching the earth's surface is inversely proportional to barometric pressure. We have also observed and recorded the variation of background with atmospheric pressure for two years. The results showed

a change of -0.11 counts/cm Hg for 5 atm. filling pressure as mentioned earlier (Figure 2.15).

The system is pumped to high vacuum, < 1 micron, between samples, hence the possibility of measurable memory effect does not exist.

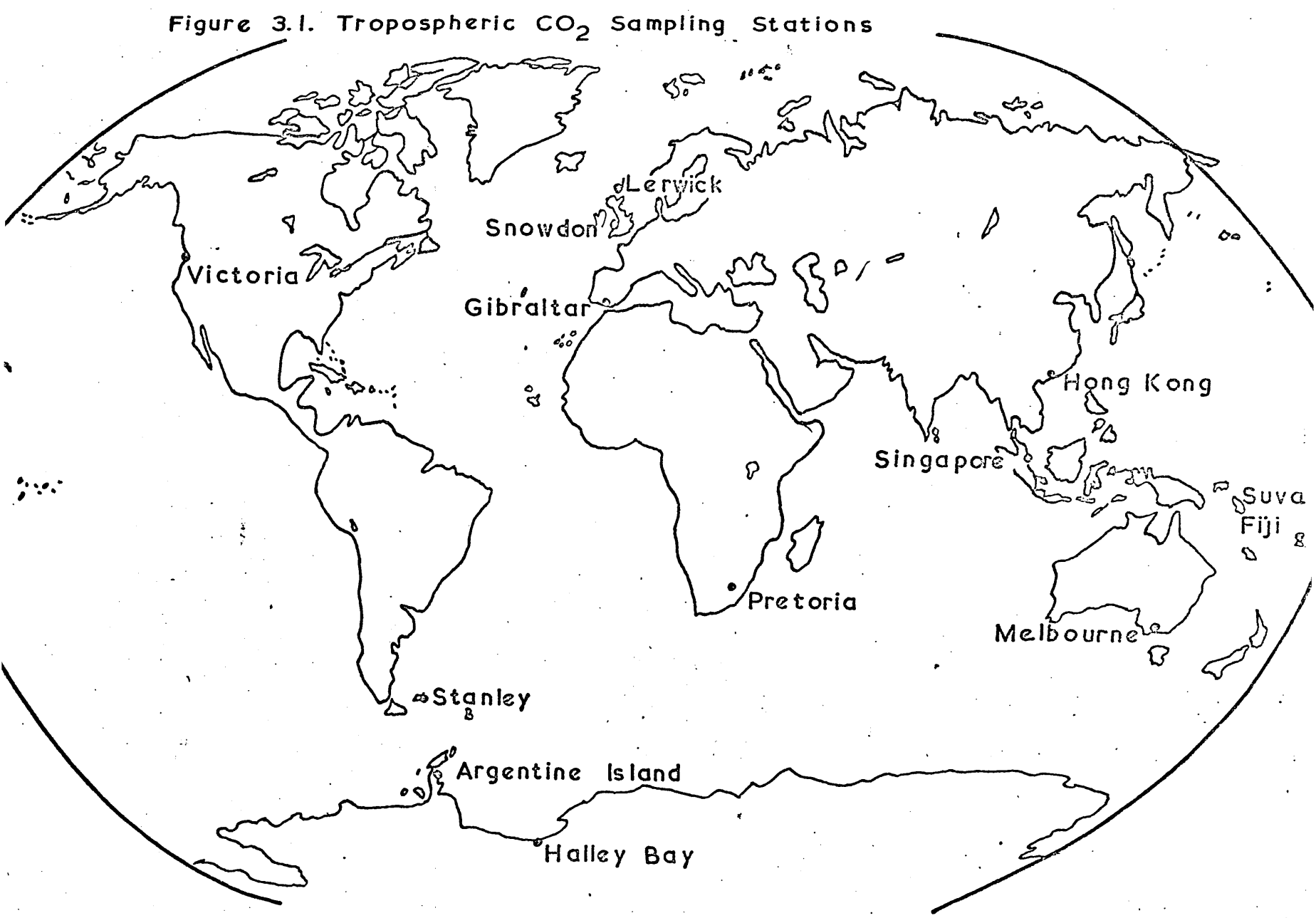
CHAPTER 3. MEASUREMENTS OF CARBON-14 IN TROPOSPHERIC CO_2

Tropospheric CO_2 samples have been collected since the beginning of 1967 at 11 stations distributed throughout both hemispheres. Sampling locations ranged from 60°N to 75°S Lat, and from 123°W to 178°E Long (Figure 3.1). These particular stations were chosen for the following reasons:

1) To permit a study of the latitudinal distribution of the "bomb" carbon-14, and an investigation of the large-scale transfer processes of CO_2 in the troposphere.
2) To allow a comparison of carbon-14 data with the results found for particulate fission products (The U.K. Atomic Energy Research Establishment, Harwell, has been measuring the activities of Sr-90, Cs-137, Ba-140, Zr-95, Ce-141, etc., in samples obtained from these same stations for several years).
3) The availability of meteorological data from most sites provided additional information for correlation purposes.
4) The sampling was being performed by reliable and qualified personnel.

Where possible sampling stations were chosen which were unlikely to be affected by local contamination from carbon-14 free CO_2 produced by fossil fuel combustion. The magnitude

Figure 3.1. Tropospheric CO_2 Sampling Stations



of the "local" Suess effect has recently been studied by Walker (B.Sc. Thesis, May 1969) who found differences of up to 18% in atmospheric carbon-14 concentrations between a rural area and an adjacent industrial centre. His study clearly illustrated the importance of the choice of a sampling site for this type of research.

The rates of exchange between various reservoirs of the carbon cycle have been estimated by several workers and, as stated previously, the results obtained from these studies showed great divergence. With the present study however it is likely that the results will be more accurate because;

1) There have been no major nuclear detonations since 1962 which would significantly affect the radiocarbon budget of the atmosphere.
2) The statistical uncertainties on the measurements of carbon-14 concentrations in current samples would be much smaller than those obtained on samples collected prior to 1961 when activities were lower.
3) With the latitudinal spread of sampling stations a much wider coverage has been obtained.

As described previously cumulative monthly collections of atmospheric CO_2 samples from each station were returned to Glasgow for carbon-14 assay. Due to restrictions of time and counting facilities every third sample was measured. Where any result was questionable the collections from adjacent months were also analysed.

3.1. Distribution of the Sampling Stations in the Northern Hemisphere and Results.

The following five stations have been established in the northern hemisphere:

(1) Lerwick,

Location:	60° 08'N Lat, 01° 11'W Long
Operator:	Meteorological Office, The Observatory.
Site description:	300 yards south-east of the Observatory, and 1.5 miles south-west of Lerwick.
Altitude:	82 m above sea level.
Wind speed:	Changes seasonally between 9 knots in summer and 17 knots in winter.
Wind direction:	Prevailing wind direction is south-west to north-east.
Sampling procedure:	The KOH solutions were exposed in the well ventilated East hut at moderate temperature.
Comment:	According to the operators report there is no possibility of a "local" Suess Effect.

Carbon-14 concentrations are shown in Table 3.1.

Table 3.1. Carbon-14 concentrations in tropospheric CO_2 collected at Lerwick (60° 08'N Lat, 01° 11'W Long).

Date of sampling	^{14}C %	^{13}C ‰	%
Jan. 1967	63.73 ± 0.75	-21.24 ±1*	62.50 ±0.80
Feb. 1967	66.62 ± 0.84	-21.24 ±1*	65.37 ±0.90
Mar. 1967	66.22 ± 0.85	-21.24 ±1*	64.97 ±0.91
Apr. 1967	69.35 ± 0.90	-21.24 ±1*	68.08 ±0.96
Jul. 1967	67.73 ± 0.85	-22.41 ±1	66.86 ±0.91
Oct. 1967	80.42 ± 1.06	-21.52 ±1	79.16 ±1.12
Nov. 1967	65.04 ± 1.14	-22.59 ±1	64.15 ±1.20
Jan. 1968	62.35 ± 1.15	-21.22 ±1	61.12 ±1.21
Apr. 1968	68.13 ± 1.18	-22.66 ±1	67.34 ±1.26
Jul. 1968	63.97 ± 0.91	-18.38 ±1	61.80 ±0.98
Oct. 1968	58.81 ± 1.00	-19.87 ±1	57.18 ±1.05

* assumed value, no mass spectrometric measurement was available.

(2) Victoria, B.C.,

Location:	48° 25'N Lat, 123° 19'W Long.
Operator:	Defence Research Establishment Pacific.
Site description:	On peninsula adjacent to Canadian Forces Base, Esquimalt.
Altitude:	About 60 m above sea level.
Wind speed:	Essentially constant throughout the year, range 9-12 knots.
Wind direction:	Prevailing south-west during January to September and north-east during October to December.
Sampling procedure:	The solutions were exposed in a covered box with gauze sides to allow free circulation of air.
Comment:	The possibility of a "local" Suess Effect from the adjacent naval base is unlikely since the operators report the prevailing wind to be directly from the ocean for more than 70% of the time.

Carbon-14 concentrations are shown in Table 3.2.

(3) Gibraltar,

Location:	36° 09'N Lat, 05° 21'W Long.

Table 3.2. Carbon-14 concentrations in tropospheric CO_2 collected at Victoria, B.C. (48° 25'N Lat, 123° 19'W Long).

Date of sampling	^{14}C %	^{13}C ‰	%
Jan. 1967	60.38 ± 0.83	-18.38 ± 1	58.27 ± 0.88
Apr. 1967	63.92 ± 0.90	-17.58 ± 1	61.49 ± 0.92
Jul. 1967	65.10 ± 0.90	-18.29 ± 1	62.88 ± 0.96
Oct. 1967	59.37 ± 0.85	-17.97 ± 1	57.13 ± 0.91
Jan. 1968	58.36 ± 0.89	-20.74 ± 1	57.01 ± 0.97
Apr. 1968	68.41 ± 1.05	-21.87 ± 1	67.36 ± 1.12
May 1968	65.99 ± 1.00	-20.27 ± 1	64.42 ± 1.07
Sep. 1968	53.54 ± 0.91	-21.81 ± 1	52.56 ± 0.95
Dec. 1968	52.97 ± 0.95	-21.49 ± 1	51.90 ± 1.03

Operator:	Meteorological Office.
Altitude:	Sea level.
Wind speed:	Changes between 10 and 15 knots according to season.
Wind direction:	Easterly and westerly.
Site description:	On the airport, R.A.F. North Front.
Sampling procedure:	The solutions were exposed in a well ventilated room adjacent to an open window.
Comment:	The urban area of Gibraltar extends from about one mile to the south of sampling site. The possibility of a "local" Suess Effect is unlikely.

Carbon-14 concentrations are shown in Table 3.3.

(4) Hong Kong,

Location:	22° 18'N Lat, 114° 10'E Long.
Operator:	Meteorological Office, Royal Observatory.
Site description:	On top of a hill, five miles north-east of the Royal Observatory.
Altitude:	1880 feet above mean sea level.
Wind speed:	Essentially constant throughout the year, range 5-7 knots.

Table 3.3. Carbon-14 concentrations in tropospheric CO_2 collected at Gibraltar (36° 09'N Lat, 05° 21'W Long).

Date of sampling	^{14}C %	^{13}C ‰	%
Jan. 1967	67.09 ± 0.80	-21.01 ± 1*	65.76 ± 0.86
Apr. 1967	67.15 ± 0.85	-21.01 ± 1*	65.82 ± 0.91
Jul. 1967	68.77 ± 1.20	-21.01 ± 1*	67.42 ± 1.28
Sep. 1967	64.92 ± 1.14	-19.01 ± 1	62.94 ± 1.20
Oct. 1967	99.05 ± 1.11	-20.35 ± 1	97.15 ± 1.18
Nov. 1967	69.14 ± 1.64	-21.57 ± 1	67.98 ± 1.69
Jan. 1968	67.79 ± 0.85	-20.12 ± 1	66.15 ± 0.91
Apr. 1968	57.41 ± 1.08	-20.39 ± 1	55.96 ± 1.16
Jul. 1968	52.59 ± 0.89	-23.16 ± 1	52.03 ± 0.95
Oct. 1968	67.00 ± 1.10	-22.29 ± 1	66.09 ± 1.17
Nov. 1968	54.04 ± 1.21	-21.21 ± 1	52.87 ± 1.30

* assumed value, no mass spectrometric measurement was available.

Wind direction:	Prevaling wind direction is easterly.
Sampling procedure:	The solutions were exposed at Tates Cairn radar station in a Stevenson screen which shelters the samples from both rain and dry deposition.
Comment:	According to the operators report there is no possibility of a "local" Suess Effect.

Carbon-14 concentrations are given in Table 3.4.

(5) Singapore,

Location:	01° 22'N Lat, 103° 59'E Long.
Operator:	Meteorological Office.
Site description:	At the airport, R.A.F. Changi.
Altitude:	Sea level.
Wind speed:	Essentially constant throughout the year, range 305 knots.
Wind direction:	Prevailing north-east to south-west during winter and south-west to north-east during summer.
Sampling procedure:	The solutions were exposed on the balcony of the Office, protected from dry deposition.

Table 3.4. Carbon-14 concentrations in tropospheric CO_2 collected at Hong Kong (22° 18'N Lat, 114° 10'E Long).

Date of sampling	^{14}C %	^{13}C ‰	%
Jan. 1967	60.38 ± 0.90	-26.29 ± 1	60.79 ± 0.95
Apr. 1967	61.17 ± 0.86	-25.51 ± 1	61.33 ± 0.92
Jul. 1967	55.16 ± 0.85	-26.25 ± 1	55.55 ± 0.89
Nov. 1967	51.07 ± 1.00	-27.01 ± 1	51.68 ± 1.12
Jan. 1968	54.04 ± 1.12	-28.06 ± 1	54.98 ± 1.21
Apr. 1968	56.57 ± 0.98	-26.15 ± 1	56.93 ± 1.05
Jul. 1968	52.58 ± 1.10	-21.44 ± 1	51.49 ± 1.18
Nov. 1968	54.71 ± 0.95	-24.39 ± 1	54.52 ± 0.97

Carbon-14 concentrations are shown in Table 3.5.

3.2. Distribution of the Sampling Stations in the Southern Hemisphere and Results.

The following six stations have been established in the southern hemisphere.

(1) Suva, Fiji Island,

Location:	18° 09'S Lat, 178° 27'E Long.
Operator:	Meteorological Office.
Site description:	About 300 yards from the coast on the windward side of the peninsula.
Altitude:	100 m above mean sea level.
Wind speed:	Varies between four and nine knots according to season.
Wind direction:	Prevailing wind direction is east to south-east.
Sampling procedure:	The solutions were exposed in one of their instrument huts.
Comment:	The Suva harbour, the nearest smoke producing centre, is on the leeward side of the peninsula. There is little possibility of a "local" Suess Effect.

Table 3.5. Carbon-14 concentrations in tropospheric CO_2 collected at Singapore (01° 22'N Lat, 103° 59'E Long)

Date of sampling	^{14}C %	^{13}C ‰	%
Apr. 1967	64.14 ± 0.84	-21.90 ± 1	63.12 ± 0.90
Jul. 1967	62.51 ± 0.94	-22.63 ± 1	61.74 ± 1.01
Oct. 1967	66.37 ± 0.90	-25.00 ± 1	66.37 ± 0.90
Jan. 1968	58.98 ± 0.83	-22.06 ± 1	58.05 ± 0.92
Apr. 1968	57.35 ± 0.83	-23.80 ± 1	56.97 ± 0.97
Jul. 1968	53.25 ± 1.10	-25.52 ± 1	53.41 ± 1.15
Oct. 1968	51.12 ± 1.14	-23.58 ± 1	50.69 ± 1.21

Carbon-14 concentrations are shown in Table 3.6.

(2) Pretoria,

Location:	25° 45'S Lat, 28° 16'E Long.
Operator:	Atomic Energy Board.
Site description:	The site is situated at Pelindaba, in a sparsely populated country. The nearest urban areas are Johannesburg and Pretoria which are respectively 36 miles south and 19 miles east of Pelindaba.
Altitude:	4200 feet above sea level.
Wind speed:	Changes between 2 and 10 knots, but for 50% of the time it remains at 5-6 knots.
Wind direction:	Prevailing between north-east and north-west.
Sampling procedure:	The solutions were exposed outdoors in a Stephanson screen which also houses meteorological instruments. The temperature was moderate throughout the year.

Carbon-14 concentrations are given in Table 3.7.

Table 3.6. Carbon-14 concentrations in tropospheric CO_2 collected at Suva (18° 09'S Lat, 178° 27'E Long).

Date of sampling	^{14}C %	^{13}C ‰	%
Jan. 1967	61.84 ± 0.85	-18.52 ± 1	59.74 ± 0.87
Apr. 1967	58.14 ± 0.85	-18.92 ± 1	56.22 ± 0.91
Jul. 1967	58.53 ± 0.90	-18.06 ± 1	56.33 ± 0.96
Oct. 1967	64.53 ± 1.18	-18.02 ± 1	62.23 ± 1.27
Jan. 1968	54.94 ± 1.10	-20.83 ± 1	53.65 ± 1.16
Apr. 1968	55.45 ± 0.90	-21.24 ± 1	54.34 ± 0.95
Jul. 1968	56.12 ± 0.92	-21.94 ± 1	55.16 ± 0.98
Oct. 1968	54.55 ± 1.00	-21.74 ± 1	53.54 ± 1.04

Table 3.7. Carbon-14 concentrations in tropospheric CO_2 collected at Pretoria (25° 45'S Lat, 28° 16'E Long).

Date of sampling	^{14}C %	^{13}C ‰	%
Jan. 1967	64.54 ± 0.89	-22.76 ± 1	63.80 ± 0.95
Apr. 1967	60.49 ± 0.83	-24.32 ± 1	60.27 ± 0.89
Jul. 1967	58.42 ± 1.04	-24.09 ± 1	58.13 ± 1.09
Oct. 1967	65.77 ± 0.85	-23.46 ± 1	65.26 ± 0.92
Jan. 1968	58.98 ± 1.14	-23.30 ± 1	58.44 ± 0.95
Apr. 1968	54.21 ± 0.87	-24.80 ± 1	54.15 ± 1.23
Jul. 1968	51.91 ± 1.25	-21.57 ± 1	50.87 ± 1.30
Oct. 1968	63.19 ± 1.01	-24.29 ± 1	62.96 ± 1.05
Dec. 1968	52.53 ± 0.85	-23.60 ± 1	52.10 ± 0.92

(3) Melbourne.

Location:	37° 49'S Lat, 144° 58'E Long.
Operator:	Meteorological Office.
Site description:	It is situated in the meteorological Office in Melbourne City.
Altitude:	Approximately 30 m above sea level.
Wind speed:	Essentially constant throughout the year, range 4-6 knots.
Wind direction:	Prevailing north-west to south-east during summer and south-east to north-west during winter.
Sampling procedure:	The solutions were exposed in a thermometer screen and a perspex protective hood was provided as protection against dry deposition.
Comment:	There are some smoke producing stacks within one mile of the site and the harbour is approximately three miles away. Therefore, there may be a slight possibility of contamination of the samples by fossil fuel CO_2.

Carbon-14 concentrations are given in Table 3.8.

Table 3.8. Carbon-14 concentrations in tropospheric CO_2 collected at Melbourne (37° 49'S Lat, 144° 58'E Long)

Date of sampling	^{14}C %	^{13}C ‰	%
Jan. 1967	55.61 ± 0.91	-25.03 ± 1	55.62 ± 0.96
Apr. 1967	56.34 ± 0.85	-26.73 ± 1	56.88 ± 0.91
Jul. 1967	51.23 ± 1.00	-20.12 ± 1	49.75 ± 1.05
Oct. 1967	52.30 ± 0.90	-21.44 ± 1	51.22 ± 0.92
Jan. 1968	52.86 ± 0.83	-19.14 ± 1	51.07 ± 0.89
Apr./May 1968	50.39 ± 1.08	-20.55 ± 1	49.05 ± 1.15
Jul. 1968	47.25 ± 1.12	-21.67 ± 1	46.27 ± 1.22
Oct. 1968	49.61 ± 1.10	-22.07 ± 1	48.73 ± 1.21

(4) Stanley, Falkland Islands,

Location:	51° 42'S Lat, 57° 52'W Long.
Operator:	Meteorological Office.
Site description:	About 2.5 miles south-east of the town and 300 yards east of the Office Building.
Altitude:	51 m above sea level.
Wind speed:	Changes between 13 and 20 knots according to season.
Wind direction:	Prevailing between north-west and south-west.
Sampling procedure:	The solutions were exposed outside in a thermometer screen which was fitted with baffles to reduce the airflow through the louvres.
Comment:	There is little industry in or near Stanley and the harbour is not at all busy. Hence a "local" Suess Effect is not expected.

Carbon-14 concentrations are shown in Table 3.9.

(5) Argentine Islands,

Location:	65° 15'S Lat, 64° 16'W Long.
Operator:	British Antarctic Survey.

Table 3.9. Carbon-14 concentrations in tropospheric CO_2 collected at Stanley (51° 42'S Lat, 57° 52'W Long)

Date of sampling	^{14}C %	^{13}C ‰	%
Apr. 1967	59.43 ± 0.84	-24.07 ± 1	59.13 ± 0.90
Jul. 1967	57.46 ± 0.79	-23.99 ± 1	57.14 ± 0.85
Oct. 1967	56.12 ± 0.79	-23.04 ± 1	55.51 ± 0.85
Jan. 1968	55.11 ± 0.98	-21.89 ± 1	54.15 ± 1.04
Apr. 1968	56.34 ± 0.78	-24.21 ± 1	56.09 ± 0.84
Jul. 1968	52.36 ± 0.84	-24.77 ± 1	52.29 ± 0.92
Oct. 1968	49.05 ± 0.96	-24.72 ± 1	48.97 ± 1.02

Site description:	At some distance from the residential camp.
Altitude:	Sea level.
Wind speed:	Changes between four and nine knots according to the season, but most of the time stays at seven knots.
Wind direction:	Prevailing wind direction is south-east to north-west.
Sampling procedure:	The solutions were exposed in a magnetic observatory at moderate temperatures.

Carbon-14 concentrations are shown in Table 3.10.

(6) Halley Bay.

Location:	75° 31'S Lat, 26° 45'W Long.
Operator:	British Antarctic Survey.
Altitude:	Sea level.
Wind speed:	Essentially constant throughout the year, range 11-14 knots.
Wind direction:	Prevailing wind direction is south-east to north-west.
Sampling procedure:	The solutions were exposed in a magnetic hut during summer and in an ozone hut during winter and both are ventilated. Moderate temperatures are maintained.

Table 3.10. Carbon-14 concentrations in tropospheric CO_2 collected at Argentine Island (65° 15'S Lat, 64° 16'W Long).

Date of sampling	^{14}C %	^{13}C ‰	%
Apr. 1967	55.44 ± 0.89	-20.40 ± 1	54.01 ± 0.95
Jul. 1967	53.87 ± 0.85	-20.97 ± 1	52.63 ± 0.91
Oct. 1967	54.66 ± 0.86	-21.43 ± 1	53.56 ± 0.89
Apr. 1968	53.20 ± 0.90	-20.93 ± 1*	51.95 ± 0.97
Oct. 1968	52.75 ± 0.86	-20.93 ± 1*	51.51 ± 0.92

* assumed value, no mass spectrometric measurement was available.

Carbon-14 concentrations are shown in Table 3.11.

3.3. Comments on Results

It will be noted from the results that during 1967-1968 the carbon-14 specific activity in both northern and southern hemispheres troposphere decreased. A seasonal variation superimposed on this overall decrease is evident in the results from stations located at northern latitudes. During the autumn of 1967 unexpectedly high values were obtained, however, from various stations in both hemispheres, the greatest divergence being shown at Lerwick and Gibraltar during October 1967. These values can possibly be ascribed to the Chinese test explosion of 17th June, 1967 (estimated yield 3 Mton) detonated at the Lop Nor testing site. This possibility is supported by the corresponding fission product measurements at these stations, reported by Atomic Energy Research Establishment, Harwell, Cambray et al (1968). The origin of these fission products can be predicted from consideration of the ratio of certain fission products. For example, if the cerium isotopes are considered ^{141}Ce, half life 32.5 days and ^{144}Ce, half life 285 days, an initial production ratio of 8.4 ($^{141}Ce/^{144}Ce$) can be calculated, Harley et al (1965). The concentrations reported for Gibraltar during October, 1967 are ^{141}Ce 0.0020 pc/Kg air and ^{144}Ce 0.0038 pc/Kg air. Some ^{144}Ce could be attributed to old debris and measurements for the previous months suggest that this contribution

Table 3.11. Carbon-14 concentrations in tropospheric CO_2 collected at Halley Bay (75° 31'S Lat, 26° 45'W Long)

Date of sampling	^{14}C %	^{13}C ‰	%
Apr. 1967	60.21 ± 1.15	-18.35 ± 1	58.08 ± 1.22
Jul. 1967	58.87 ± 0.94	-19.25 ± 1	57.04 ± 1.01
Oct. 1967	58.36 ± 0.79	-19.53 ± 1	56.63 ± 0.85
Dec. 1967	55.78 ± 0.85	-19.97 ± 1	54.21 ± 0.91
May 1968	55.27 ± 0.90	-28.27 ± 1	56.44 ± 0.96
Jul. 1968	55.13 ± 1.02	-22.01 ± 1	54.20 ± 1.12
Oct. 1968	52.19 ± 1.00	-22.92 ± 1	51.56 ± 1.05

might be about 0.0009 pc/Kg air. Consideration of the test schedule indicates that there would be negligible quantities of ^{141}Ce from these sources, and this is confirmed by the earlier collections. Therefore, the activity ratio of $^{141}Ce/^{144}Ce$ can be estimated at 0.69 for October, 1967. This corresponds to debris produced about 3.5 months previously. The divergence at Lerwick during October, 1967 can be explained in the same manner.

The measured increase in the tropospheric carbon-14 and fission products probably arise from the injection of this Chinese "bomb" carbon-14 due to mixing associated with localised meteorological conditions. Such phenomena, occurring on a local basis and involving the passage of a frontal zone derived from tropopause folding, have been described by Danielsen (1965).

In a similar manner, the increase in carbon-14 concentrations observed in the results from Pretoria during October, 1968 may be attributed to the French test of 24th August, 1968 which occurred in the southern hemisphere - yield 2 Mton.

The carbon-14 activities in Melbourne samples are generally low. The reason for this, as described above, may be a "local" Suess Effect. The same effect was observed by Rafter (1965) on the previous years' carbon-14 data.

As to the $\delta^{13}C$ values, in general they are relatively high compared to the normal value of about -9‰ for atmospheric CO_2, Craig (1953). It was demonstrated by Craig (1953) that the absorption of atmospheric CO_2 in basic solutions could cause significant isotopic fractionation. Since we exposed 8N KOH

solution to the atmosphere for collection of CO_2 samples the magnitude of the fractionation observed could not be predicted. It is interesting to note, however, that the results fall in the same range as those reported by other workers using similar collection techniques, Olsson and Stenberg (1967), Rafter (1965).

The small variations between $\delta^{13}C$ values may be due to (1) temperature changes prevailing during the sample collection, (2) dilution of the atmospheric CO_2 by local Suess effect, or (3) treatment in the laboratory.

It is also interesting to note that the change in the mean $\delta^{13}C$ values of Halley Bay samples for 1968 relative to the previous year corresponds to a reported change of sampling site of several miles. However, the general sampling technique remained unchanged.

CHAPTER 4. QUANTITY AND DISTRIBUTION OF ARTIFICIAL CARBON-14 IN THE ENVIRONMENT

The dispersal of artificial carbon-14 began with the explosion of the first nuclear device in 1945. During the period 1945-1954 the quantity of carbon-14 produced by nuclear explosions was small due to the relatively low neutron yields of the fission devices. From 1955 to 1960 considerable amounts of carbon-14 were produced by higher yield thermonuclear detonations and during 1961-1962 the period of most extensive testing, the quantity of artificial carbon-14 introduced into the stratosphere was almost three times the amount produced prior to that time. From the end of 1962 to 1967 there were no major atmospheric tests but during 1967-1968 Chinese and French high yield detonations, with a total yield of about 15 Mton, have certainly added further artificial carbon-14 to the carbon cycle. These quantities are not significant, however, when compared with the total yield of 337 Mton of the 1961-1962 tests (Table 4.1).

Due to the extensive testing by the major powers in 1961 and 1962 significant amounts of artificial carbon-14 were introduced into the stratosphere. As a result of the transport of $^{14}CO_2$ between the stratosphere, the troposphere and the ocean this carbon-14 has been distributed throughout the reservoirs and more accurate measurements of carbon-14 concentrations in these reservoirs are now possible. With these new data, therefore,

Table 4.1. Fission and fusion energy yields of nuclear tests (1945-1969)

Period	Fission yield (Mton)		Fusion yield (Mton)	
	Air tests	Surface tests	Air tests	Surface tests
1945-51	0.19	0.57	-	-
1952-54	1.0	37.0	-	22.0
1955-56	5.6	7.5	5.4	9.5
1957-58	31.0	9.0	26.0	19.0
1959-60		Test Moratorium		
1961	25.0	-	95.0	-
1962	76.0	-	141.0	-
1963-68	0.3	0.1	15.0	-
Totals	139.09	54.17	282.4	50.5

improved calculations may be made of the inventory of carbon-14 in the reservoirs and assessments of the various exchange parameters performed more accurately.

Since 1962 the excess carbon-14 content of any reservoir of the carbon cycle has varied considerably with time. A method of calculating the inventory of artificial carbon-14 in a particular reservoir would involve a knowledge of the quantity of carbon-14 introduced into the atmosphere by nuclear explosions and the rate of exchange of carbon-14 (via CO_2) between the various reservoirs. Since these factors, especially the exchange rates are not known accurately, attempts will be made to calculate the distribution of artificial carbon-14 from experimental observations of excess carbon-14 in the various reservoirs. These results can then be compared with the estimated inventory from the energy yield of nuclear tests.

The magnitude of the exchange rates of CO_2 between various reservoirs, especially between the atmosphere and the oceans has particular significance for the carbon-14 dating method since the $^{14}C/^{12}C$ ratio in the atmosphere is largely controlled by these factors. Values of the exchange rates, calculated from earlier measurements, were inconsistent and covered a wide range (for example, the residence time of CO_2 in the atmosphere before transfer to the ocean has been variously estimated to be from 2 to 25 years as shown in Table 1.3). It is assumed that this diversity of data was partly due to the assumptions made regarding reservoir sizes and partly due to the inhomogeneities in carbon-14 distribution throughout the reservoirs.

4.1. Observations of Tropospheric Carbon-14 Concentrations and Their Interpretation.

As mentioned previously monthly CO_2 samples were collected during 1967 and 1968 at eleven stations distributed latitudinally throughout the world and their carbon-14 concentrations were measured in the laboratory. Concentrations, corrected for fractionation, were expressed relative to the carbon-14 activity of the National Bureau of Standards oxalic acid standard. The results were shown in Tables 3.1 - 3.11.

From considerations of the periodical variations of carbon-14 concentrations in the troposphere, due to uptake by the ocean and biosphere, and the seasonal dependence of carbon-14 transport from the stratosphere it was believed that the variation with time of carbon-14 activities could best be described by a function of the type:

$$y = A + Be^{-bt} + Ce^{-ct} \text{ Sin } \left[2\pi (t - to) \right]$$

This function was applied to the observations at various latitudes and the best values for the parameters A, B, C, b, c and t_o were found.

The method used for the determination of the parameters involves the principle that the sum of the squares of the deviations of the observations from the predicted curve (best fit line) should be a minimum.

Thus $$f(A,B,C) = \sum \left[A + Be^{-bt_i} + Ce^{-ct_i} \text{ Sin } (2\pi (t_i - t_o)) - y_i \right]^2 \rightarrow 0.$$

In this treatment b, c and t_o are first given estimated values

and the computer programme permits the calculation of f(A,B,C) for various combinations of b and c and a fixed t_o. The minimum value for f(A,B,C) can be established by inspection from the computed results (See Appendix B). The results of these calculations for each sampling station are shown in Table 4.2 and the curves described by the function for nine of the stations are shown in Figures 4.1 - 4.9. The observed carbon-14 concentrations for the remaining two stations in the southern hemisphere, Argentine Islands (65°S) and Halley Bay (75°S), did not show any seasonal variations and seemed to decrease linearly with time. The straight lines obtained via computer regression analysis (See Appendix A) for these stations are shown in Figures 4.10 and 4.11.

Examination of the data indicates that the carbon-14 variations at Lerwick (60°N), Victoria B.C. (48°N) and Hong Kong (22°N) are in phase, showing peak values during the spring months of both 1967 and 1968. In 1967 the carbon-14 concentrations at Victoria B.C. and Hong Kong declined with about the same gradient following the spring peak, whereas at Lerwick they showed a lower gradient. A more rapid increase and decrease in carbon-14 levels was observed at Victoria B.C. than at either Lerwick or Hong Kong during the spring - summer of 1968. The seasonal change at this station, (10%), was also the largest of all observations in the northern hemisphere. An explanation for this may be that some carbon-14 was being contributed by the June 1967 high yield (3 Mton) Chinese nuclear test in central Asia. This possibility is supported by the occurrence

Table 4.2. Values of parameters in the function,
$y = A + Be^{-bt} + Ce^{-ct} + \sin(2\pi(t-t_o))$, $(t_o = 0.05y)$

	A	B	C	b $year^{-1}$	c $year^{-1}$
Lerwick	-1.53×10^{-5}	65.13	2.63	2.75×10^{-2}	1.0×10^{-4}
Esquimalt	-1.32×10^{-4}	60.23	48.83	2.2×10^{-2}	1.0×10^{-4}
Gibraltar	-5.05×10^{-3}	71.36	-1.69	0.15	0.09
Hong Kong	5.67×10^{-4}	57.88	7.17	0.047	0.9
Singapore	9.22×10^{-4}	71.37	-7.66	0.18	1.54
Suva	1.24×10^{-4}	60.82	-4.82	0.075	0.69
Pretoria	5.55×10^{-5}	65.11	-4.35	0.105	2.0×10^{-4}
Melbourne	2.51×10^{-4}	53.44	15.81	0.063	3.70
Stanley	-1.09×10^{-4}	60.22	1.44	0.088	5.0×10^{-5}

Figure 4.1. Variations of Carbon-14 Concentrations at Lerwick (60°08'N)

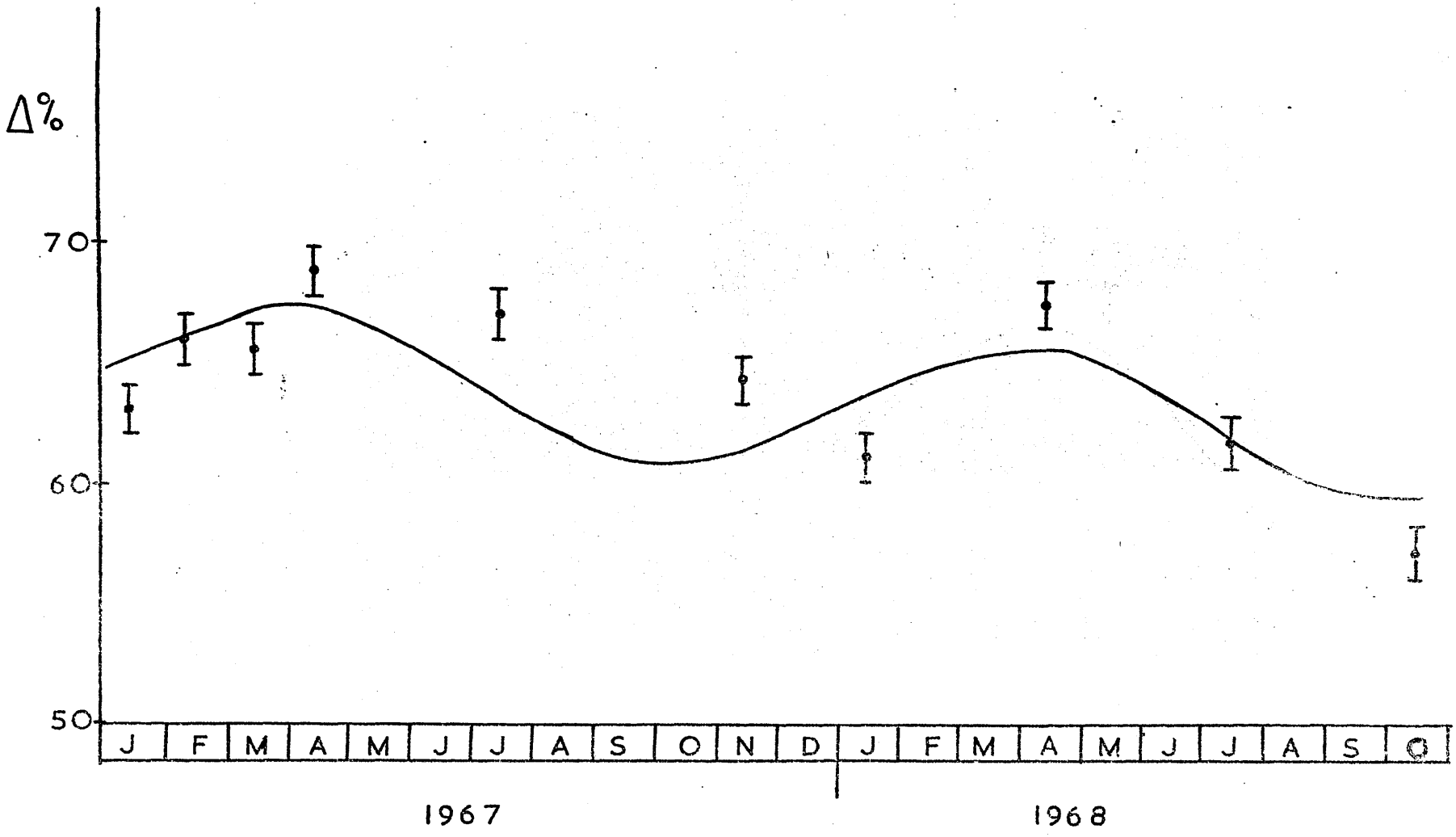


Figure 4.2. Variations of Carbon–14 Concentrations at Esquimalt (48°25'N)

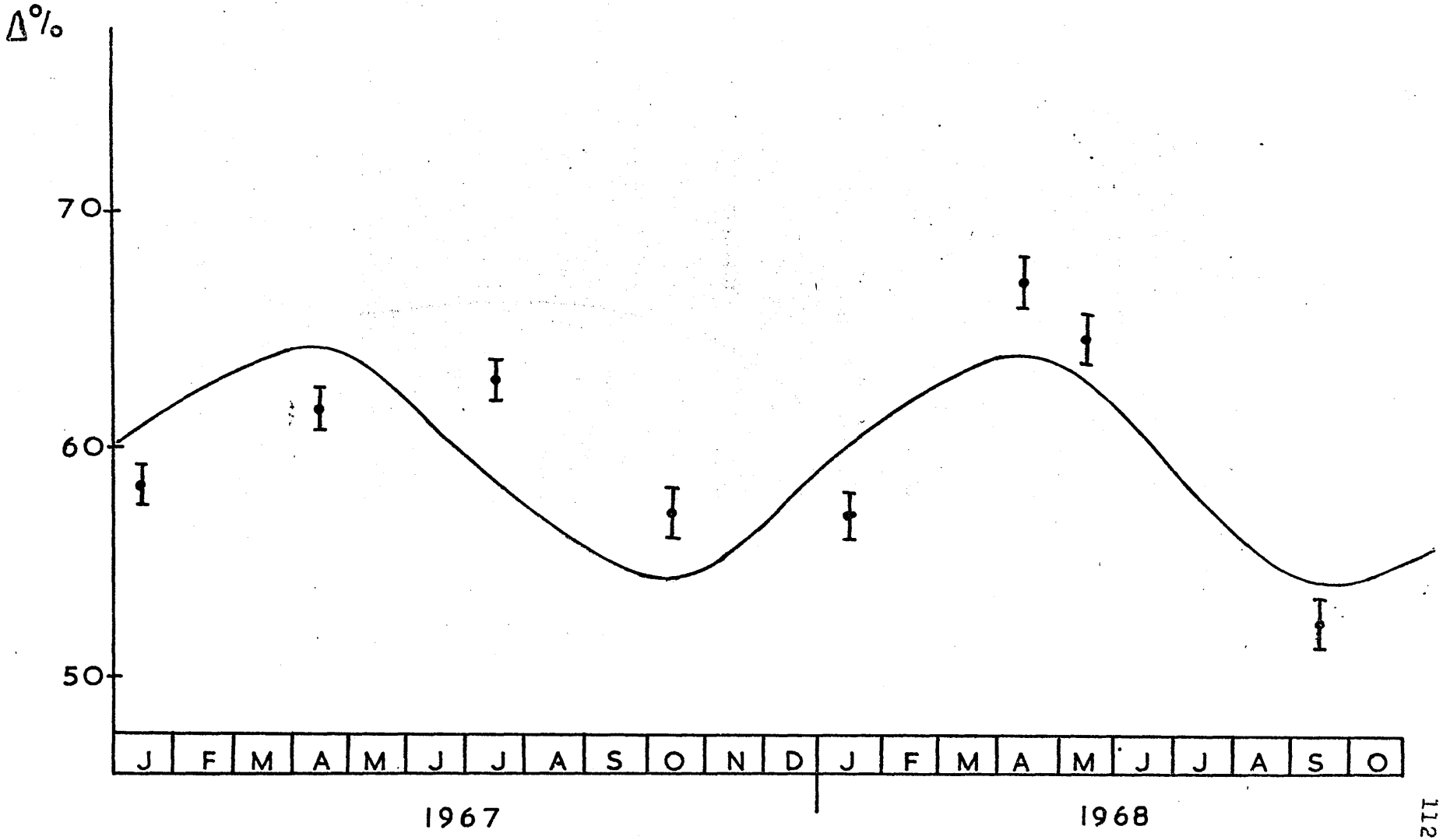


Figure 4.3. Variations of Carbon—14 Concentrations at Gibraltar (36°09'N)

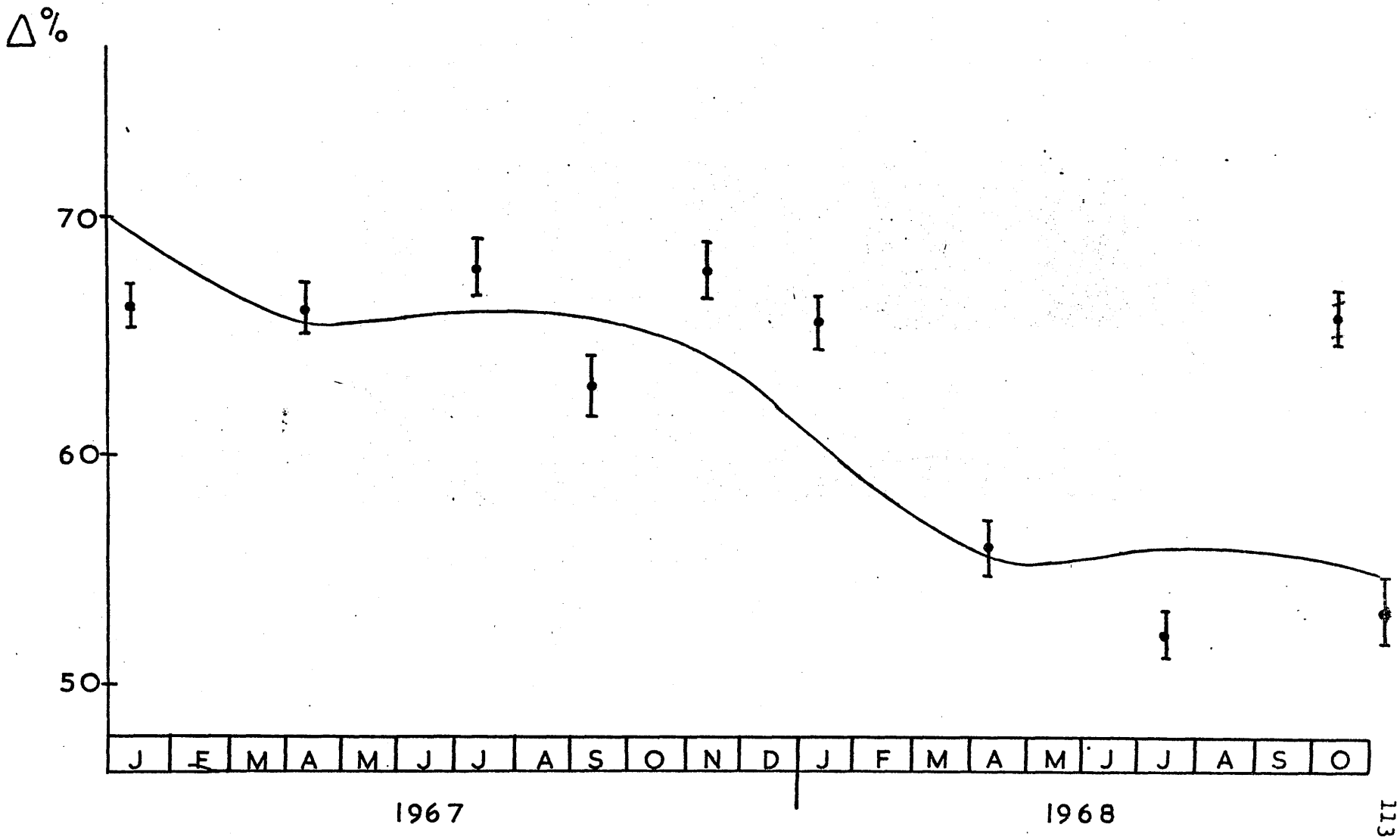


Figure 4.4. Variations of Carbon-14 Concentrations at Hong Kong (22°18'N)

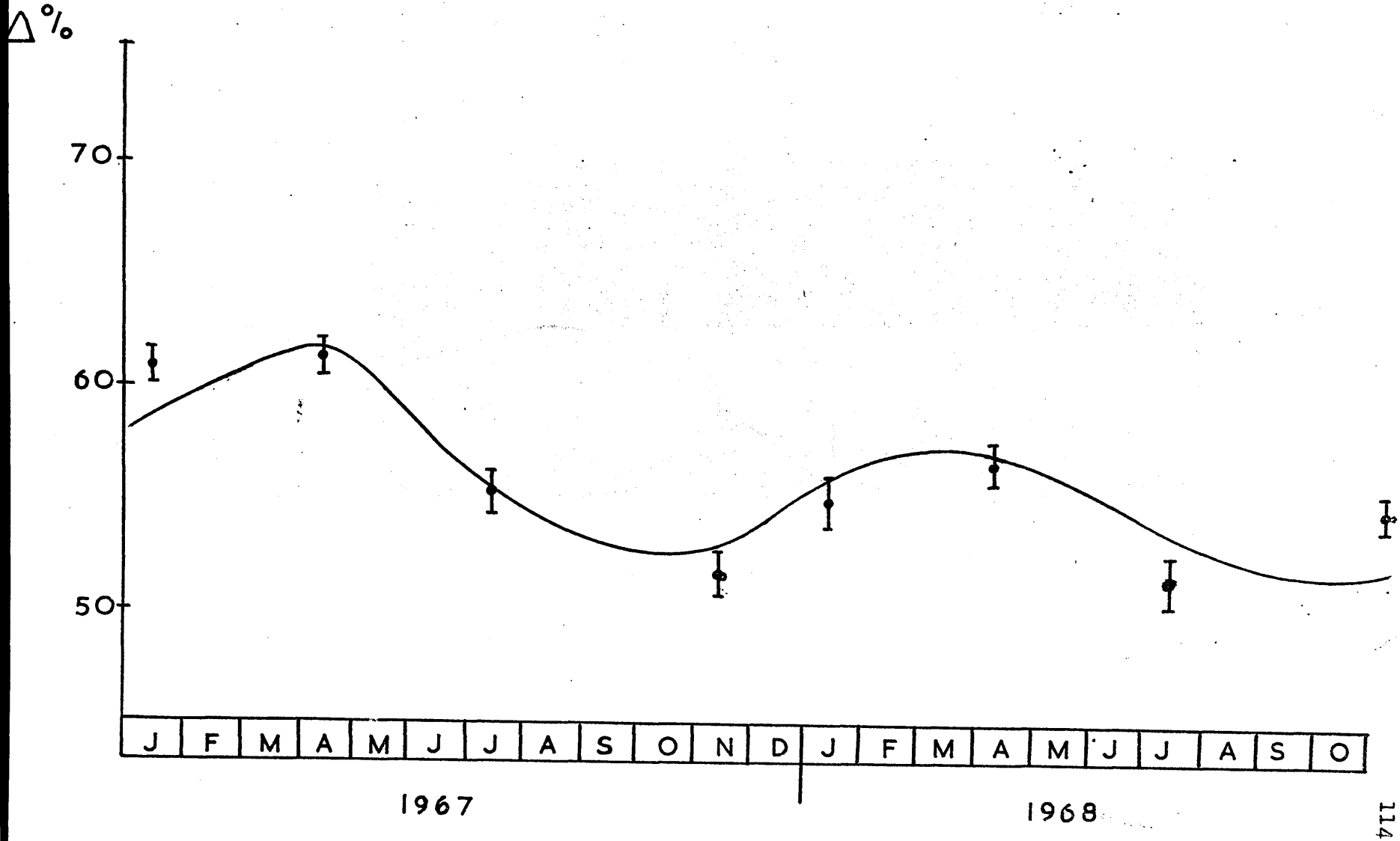


Figure 4.5. Variations of Carbon—14 Concentrations at Singapore (01°22'N)

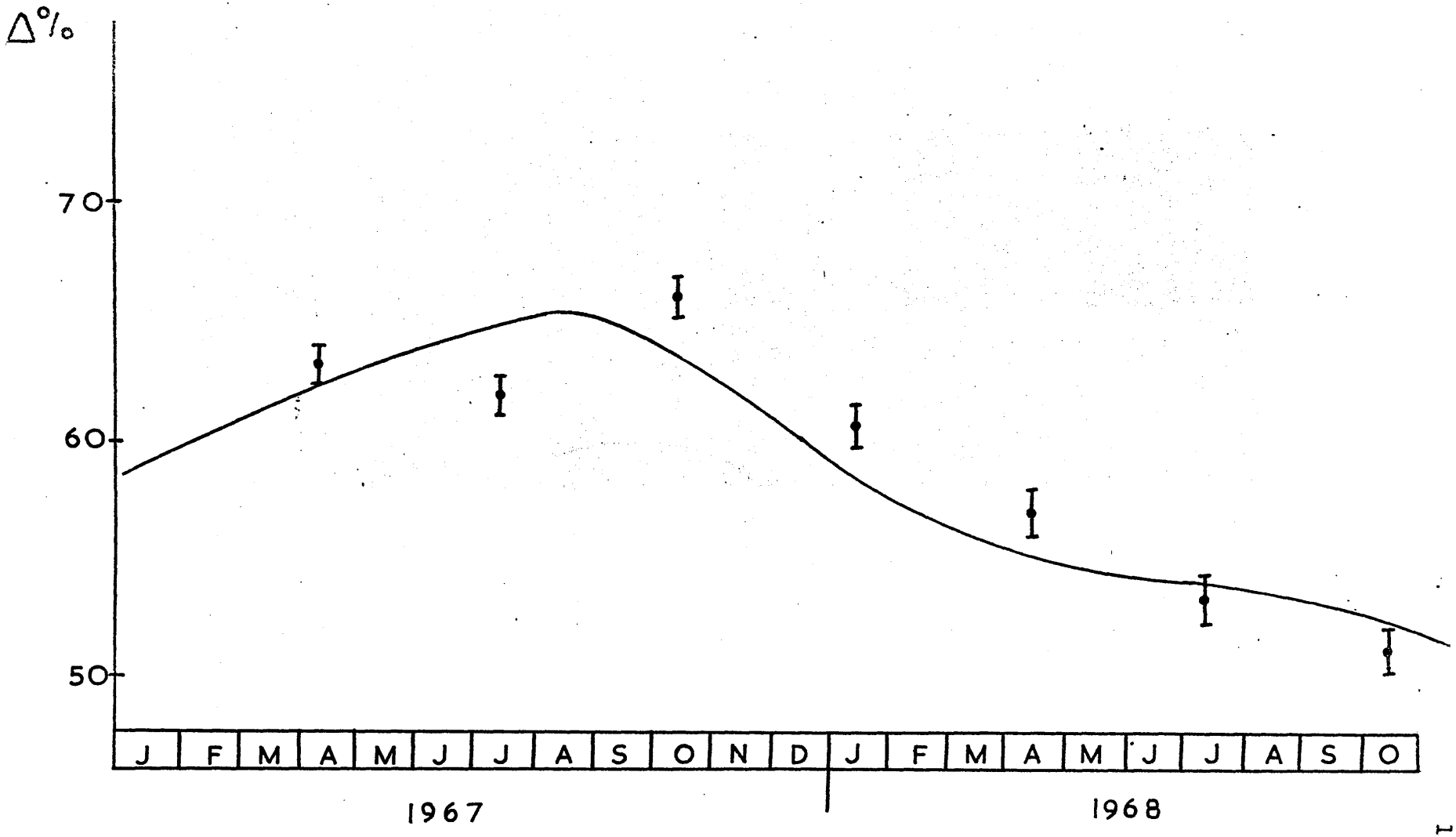


Figure 4.6. Variations of Carbon-14 Concentrations at Suva, Fiji (18°09' S)

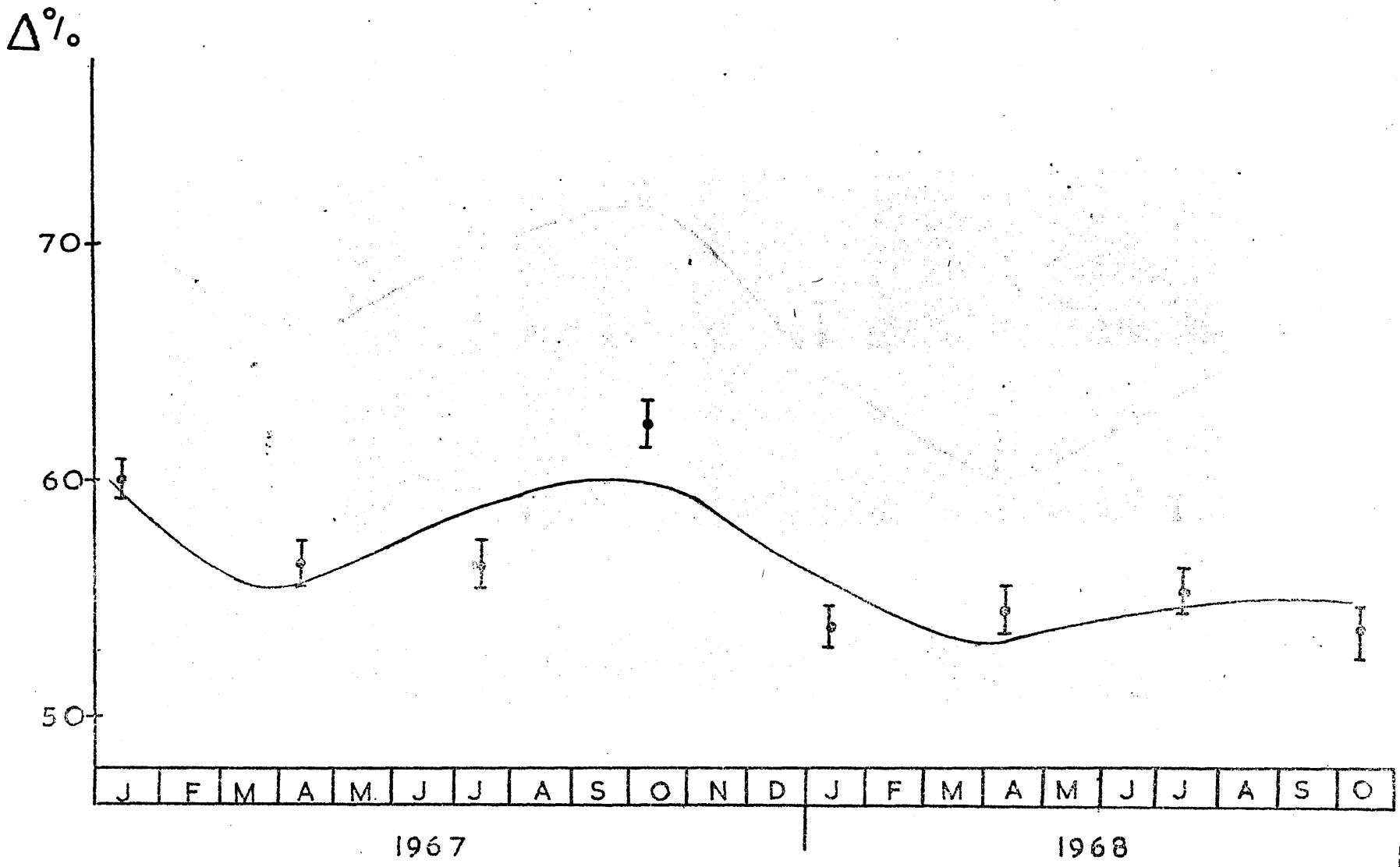


Figure 4.7. Variations of Carbon-14 Concentrations at Pretoria (25°45' S)

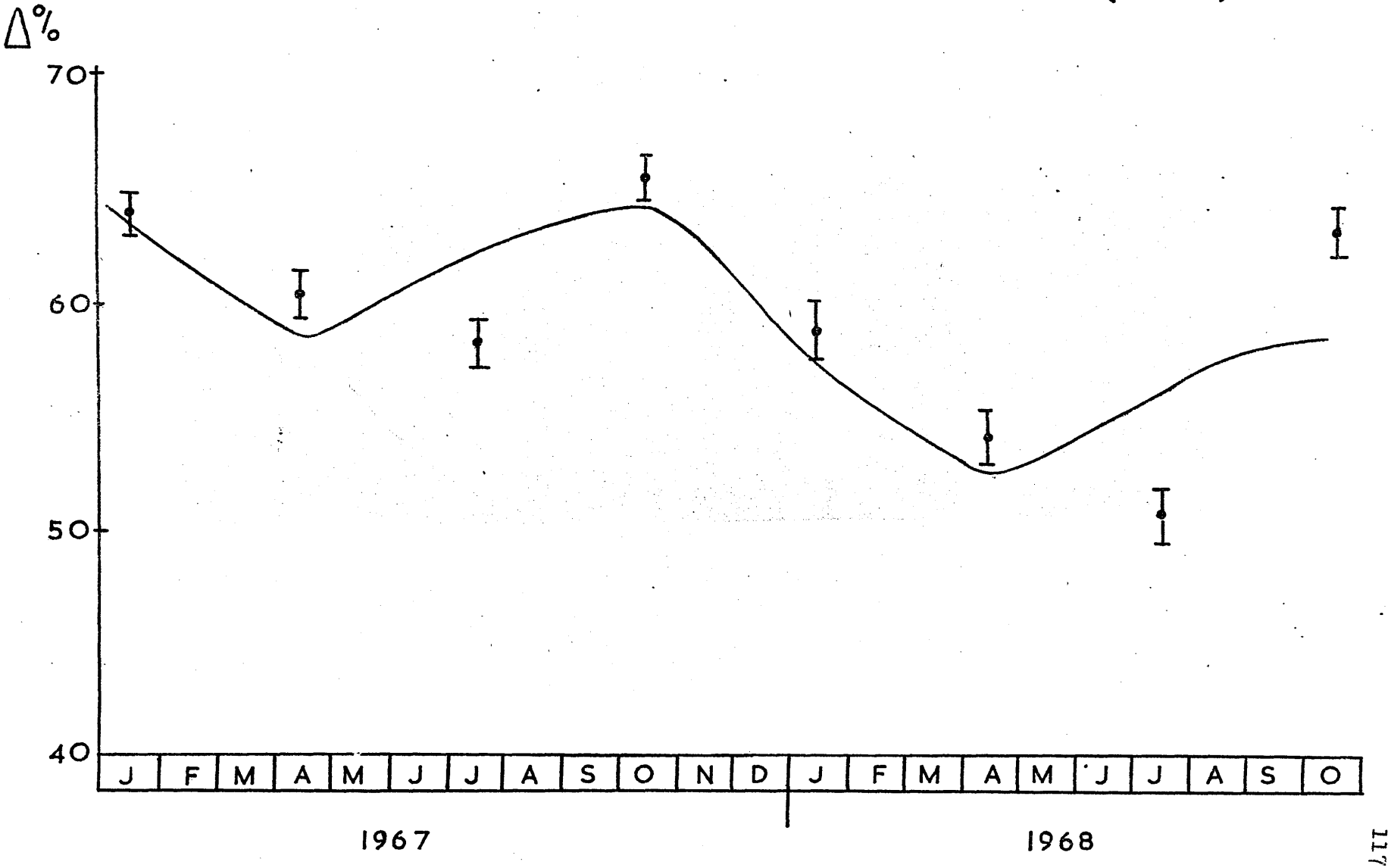


Figure 4.8. Variations of Carbon-14 Concentrations at Melbourne (37°44'S)

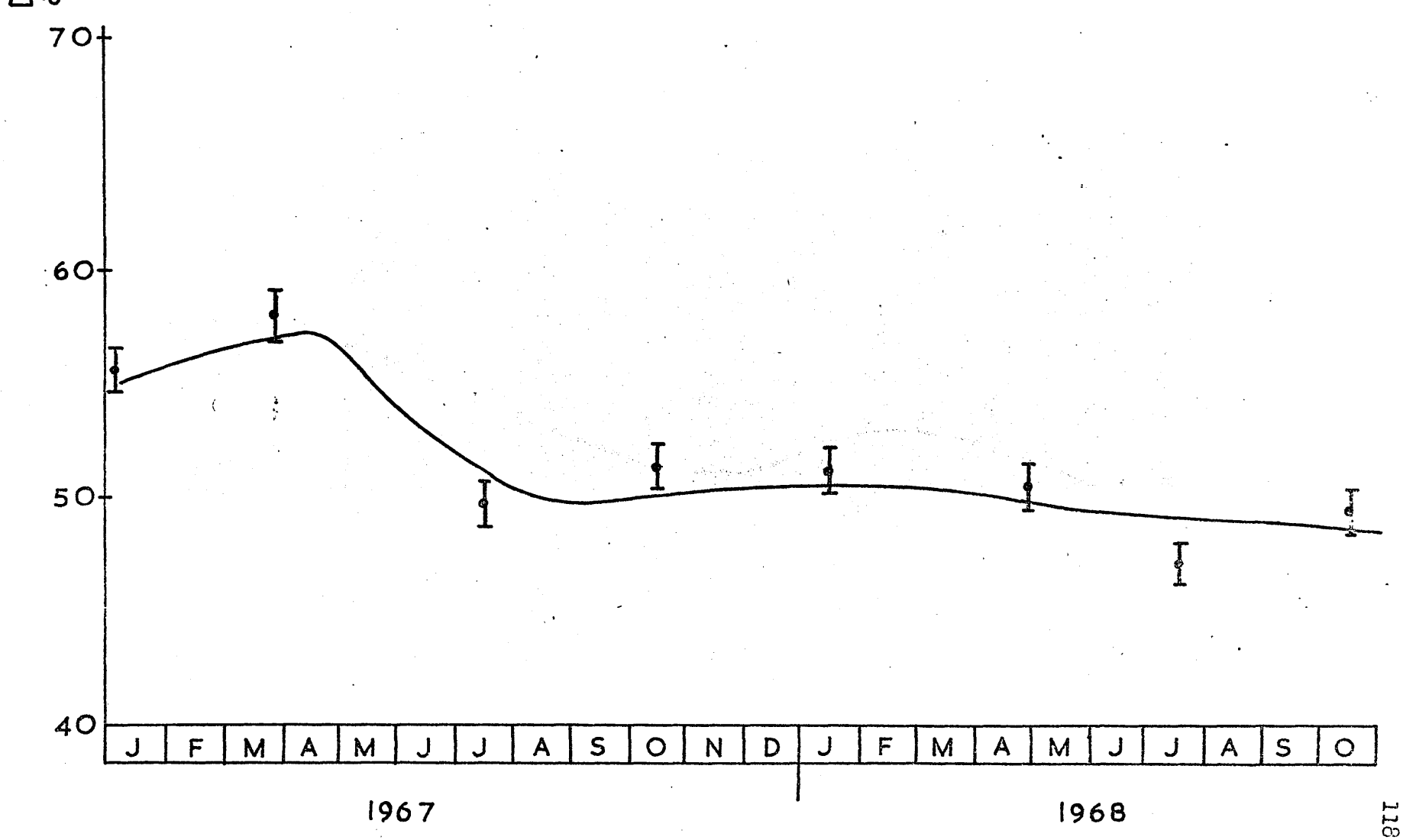


Figure 4.9. Variations of Carbon-14 Concentrations at Stanley (51°42'S)

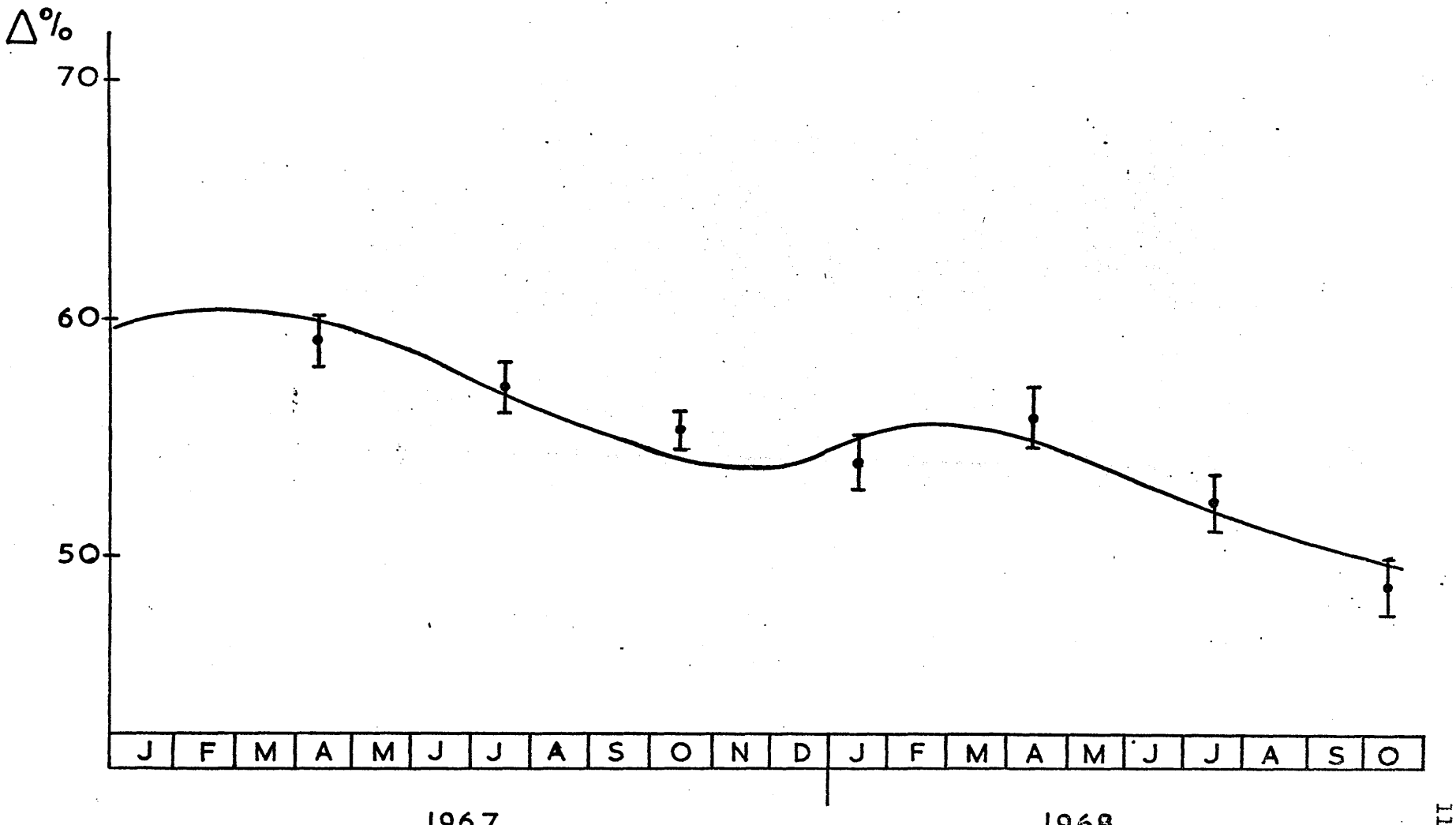


Figure 4.10. Variations of Carbon-14 Concentrations at Argentine Island (65° 15' S)

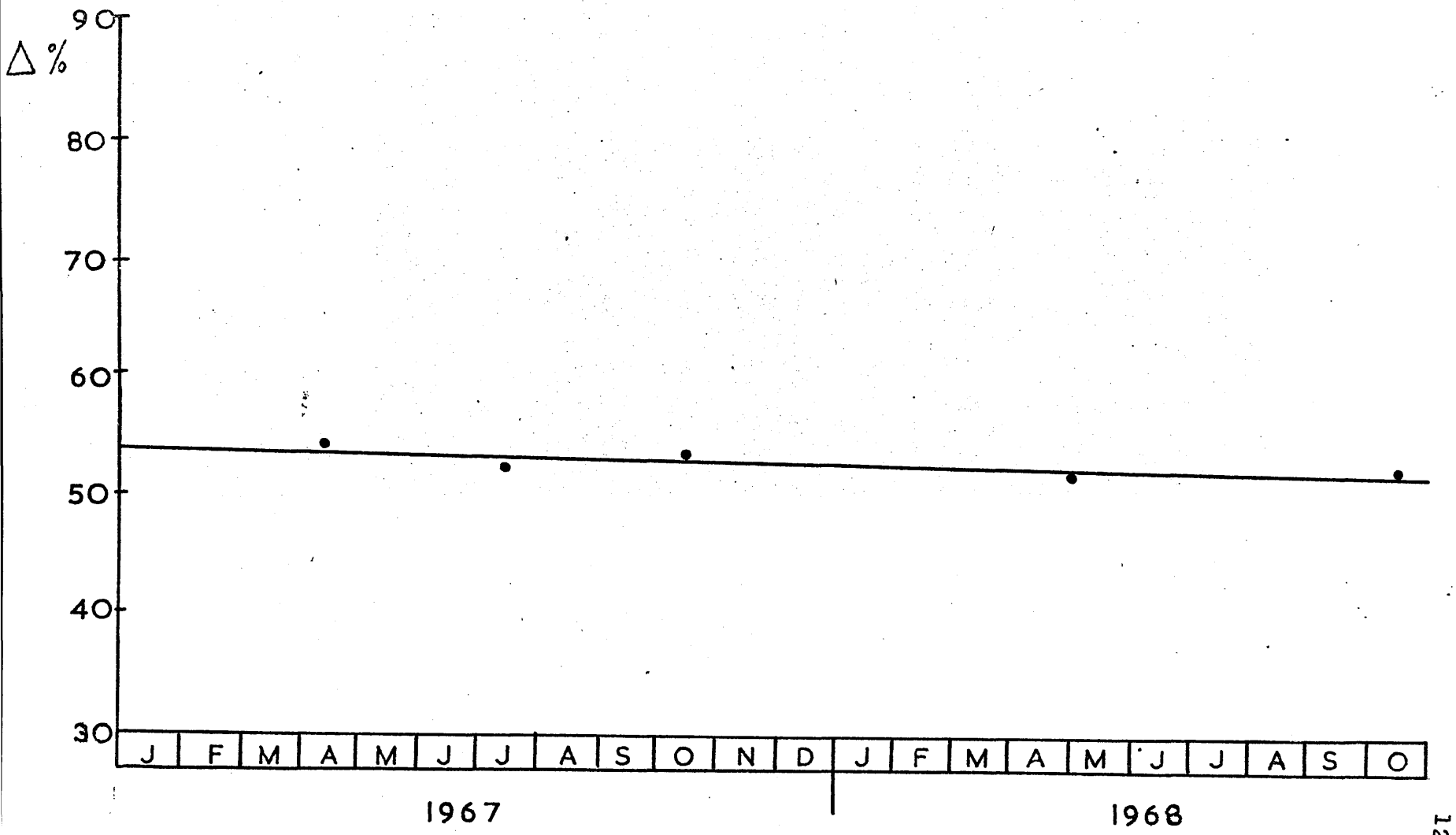
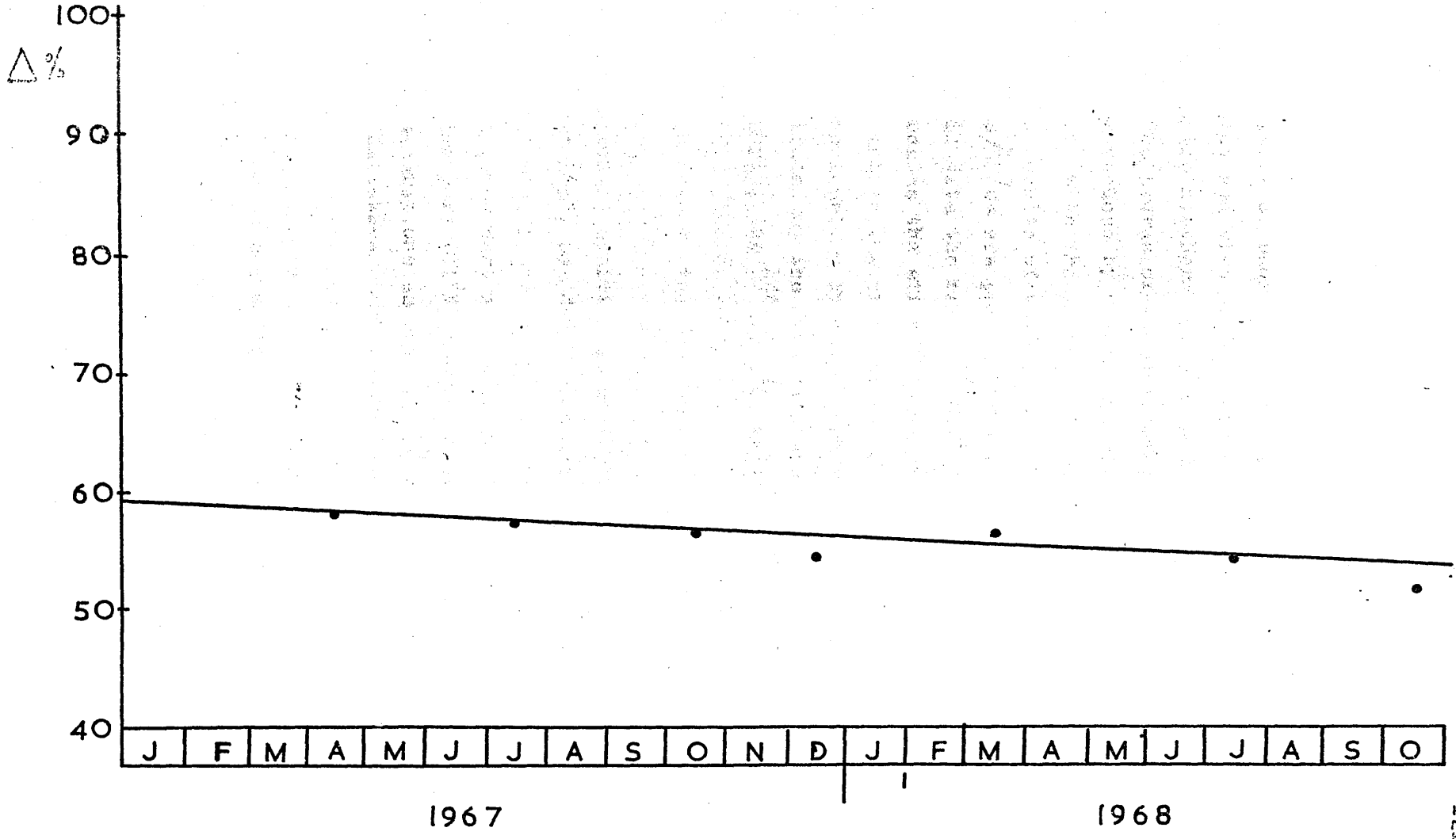


Figure 4.11. Variations of Carbon-14 Concentrations at Halley Bay (75° 21' S)



of increased activity of short-lived fission products in air at the same station and also most of the other stations at mid-latitudes in the northern hemisphere during the first half of 1968. The source of these short-lived fission products might be deduced by comparison of the ratios of pairs of fission products with the value of these ratios at the time of fission. The results of Cambray et al (1968, A.E.R.E report) for $^{144}Ce/^{137}Cs$ are particularly useful in this respect. According to their data the ratio $^{144}Ce/^{137}Cs$ increased from August 1967 onwards as the sixth Chinese explosion of 17th June 1967 contributed increasing proportions of the short-lived activity at ground level. By mid - 1968 equal proportions were being contributed by the June explosion and by older debris. For example, the $^{144}Ce/^{137}Cs$ ratios in ground-level air at Victoria, B.C. increased from 2.1 to 6.1 during the first half of 1968 despite the fact that no explosion occurred during this time.

The peak carbon-14 activity at Singapore ($01^{\circ}N$), which appeared in August 1967, was delayed relative to the peaks of the other northern hemisphere stations. This delay was maintained in the declining part of the curve throughout the year. Interestingly, Singapore ($01^{\circ}N$) showed almost the same variations in carbon-14 concentrations as Suva ($18^{\circ}S$) and Pretoria ($25^{\circ}S$) in the southern hemisphere. This suggests that either the resistance to hemispheric transfer is at more northerly latitudes, or that if the mixing is predominantly across the equator it is extremely rapid. On this question it is exceedingly interesting

to examine some of the data on particulate fission-product transport. Palmer (1969) has recently investigated inter-hemispheric transport in a study of the fission products produced by the French tests of July 1968 in the southern hemisphere. He found that the time of transfer of ^{131}I and ^{140}Ba across the equator was not more than three weeks. Cambray et al (1968) also reported that significant concentrations of short-lived radioactive debris from French tests of July 1968 crossed the equator and were detected at Hong Kong during the second half of August 1968. Although the fission products may not be representative indicators of vertical transport of air they are very useful tracers of horizontal movement. It is not too surprising, therefore, to observe similarities in the behaviour of carbon-14 in the atmosphere for stations $20^{\circ}N$ - $20^{\circ}S$.

The observed activities at Gibraltar ($36^{\circ}N$) showed an irregular pattern. The spring peak appeared in July 1967 with a value of 68.11% above the natural level, and a very high activity (97.15%) was observed during October 1967 (the possible cause for this was explained in Chapter 3). Again the observed activity in November 1967 was as large as the July peak value. During 1968 the spring peak did not appear, but again in October 1968 a rather high activity relative to adjacent months was observed. No explanation has been found for this peak activity so far. On fitting the curve these two October values were neglected. These irregular perturbations of carbon-14 activity at Gibraltar seem to agree with some of the findings of Lal and Rama (1965). These authors examined the tropospheric data of

Kusumgar (1963) and Nydal and Lövseth (1965), and discovered that the carbon-14 concentrations in the belt 30 ± 5°N showed comparatively higher and more random fluctuations than at all other latitudes. From these observations they postulated that a barrier to horizontal transport existed at 30°N and thus they constructed four cells in their tropospheric model for the evaluation of interhemispheric exchange rates.

In the southern hemisphere, Suva (18°S) and Pretoria (25°S) showed peak values in Spring 1967 and 1968 which may be ascribed to the spring input from the stratosphere of the southern hemisphere. Such a postulate is less likely, however, because of the absence of corresponding peaks at the stations in mid-latitudes, where maximum injection from the stratosphere is expected. It is more probable that peaks are a result of the diffusion of carbon-14 from higher latitudes in the northern hemisphere through the equatorial regions.

The carbon-14 activities at Melbourne (37°S) and Stanley (51°S) differ markedly from those at Suva and Pretoria in such a way that the peak concentrations lag in time and are diminished in size. One reason for this could be a net southward transport of carbon-14 from the 0-30° south region and greater uptake by the larger ocean surface area south of 30°S. The effect of the oceans could be important in that they act as a sink which absorbs CO_2 from the troposphere with a high carbon-14 concentration and returns CO_2 with a lower carbon-14 concentration. Therefore the overall result of exchange with the oceans is a dilution of the tropospheric carbon-14 concentration.

Further south the seasonal variations of carbon-14 activity have completely disappeared as can be seen in the data from Argentine Islands (65°S) and Halley Bay (75°S). The disappearance of seasonal variations towards the southern polar regions also implies that the transport from the stratosphere may be slower in these areas and that the carbon-14 is mainly transferred from the northern hemisphere troposphere.

Since all large scale injections of artificial carbon-14 have been in the northern hemisphere stratosphere, the observed higher carbon-14 concentrations in the troposphere of the northern hemisphere, compared to the southern hemisphere, were expected. A comparison of northern and southern hemisphere results shows much greater fluctuations in the northern hemisphere particularly above 30°N latitude.

Since the residence time of artificial carbon-14 in the troposphere is greater than the mixing time of the troposphere between the hemispheres (as will be shown later) a marked tropospheric latitudinal effect in either hemisphere would not be expected. The observations, however, do suggest a latitudinal dependence of carbon-14 transfer from stratosphere to troposphere, which is more visible in the northern hemisphere. For example, the measurements of carbon-14 activities at various latitudes for April 1968: 60°N - 65.4%, 48°N - 63.2% and 22°N - 56.5% are most likely associated with the rapid spring entry of carbon-14 into the troposphere by a mechanism similar to fission product transport. Tauber (1961) has reported latitudinal variations in the descent of bomb-produced carbon-14 from the stratosphere

to the troposphere as deduced from the carbon-14 activities of Danish cereals (56°N) and of atmospheric CO_2 (25° - 40°N). Tauber has also postulated that the latitudinal variations might have contributed substantially to the short-term oscillations in the carbon-14 activity of tree-rings and in addition might account for the minor differences found in the carbon-14 activity of plant material from different locations. Changes in cosmic ray flux or changes in the exchange rate of CO_2 between the atmosphere and the ocean cannot explain all of the geographical variations.

The general trend of atmospheric carbon-14 concentrations, however, is that the seasonal fluctuations diminished in 1968, and the carbon-14 activities in both northern and southern hemisphere declined during 1967 and 1968 with mean gradients of -0.48% per month and -0.30% per month respectively. Extrapolation of the data in figures 4.1 - 4.11 to 1969, suggests that the entire troposphere has reached a fairly uniform carbon-14 concentration in a period of seven years since the cessation of major nuclear testing.

4.2. Calculations of the Global Inventories of Artificial Carbon-14 (1967 and 1968)

The quantity of artificial carbon-14 in the various reservoirs has been calculated for July 1967 and for July 1968.

In these calculations a value of 74×10^5 ^{14}C atoms/g air has been taken as the natural atmospheric level, as calculated by Hagemann et al (1965) assuming that the specific

activity was 13.1 dpm $^{14}C/g$ carbon prior to nuclear testing.

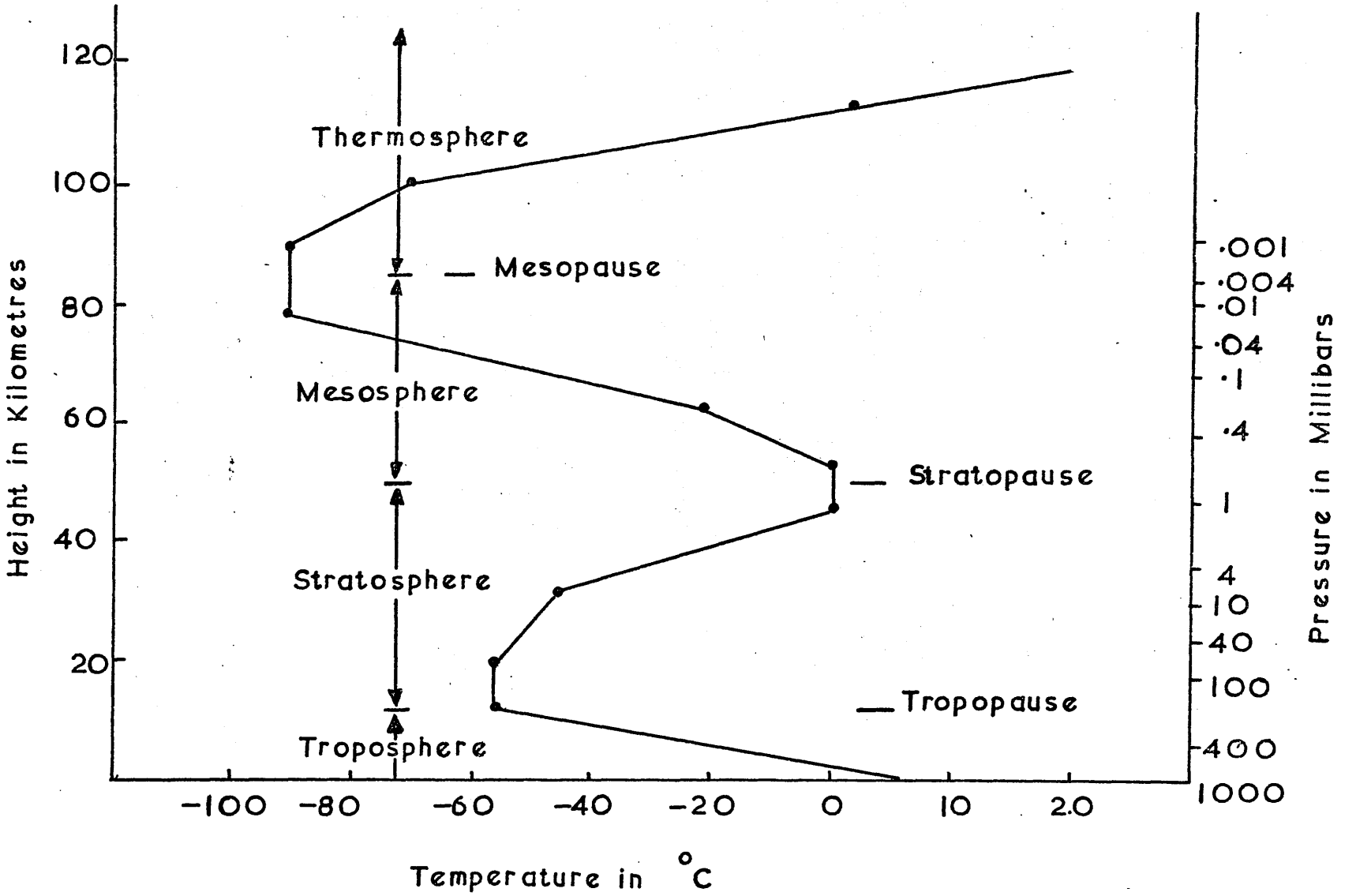
Before proceeding to the inventory calculation it is necessary to define the various carbon reservoirs and their boundaries which have been used in this calculation.

The atmosphere is conveniently subdivided into regions according to temperature or composition, and the dynamic processes involved. The vertical temperature structure is characterized by alternate regions of decreasing and increasing temperature. According to this structure the atmosphere is divided into the troposphere, stratosphere, mesosphere and thermosphere (Figure 4.12). In this study we will mainly be concerned with the troposphere and stratosphere.

The troposphere is the lowest region, where the temperature decreases with increasing height. It contains approximately two-thirds of the mass of the atmosphere. Most of the weather features - cloud and precipitation - occur in this region. The average rate of decrease of temperature with height in this region is about $6^{o}C/km$.

The tropopause is the boundary between the troposphere and the stratosphere above which the temperature gradient is reversed from that in the troposphere. Formerly considered to be a single pole-ward sloping plane, this boundary is now recognized as consisting of several overlapping layers, a series of tropopauses usually separated by jet streams. Its height may drop from nearly 18 km in the tropics to about 8 km in polar regions. It is higher in summer than in winter for any given latitude. In the "standard atmosphere" the mean

Figure 4.12. Vertical Temperature Distribution in the Atmosphere



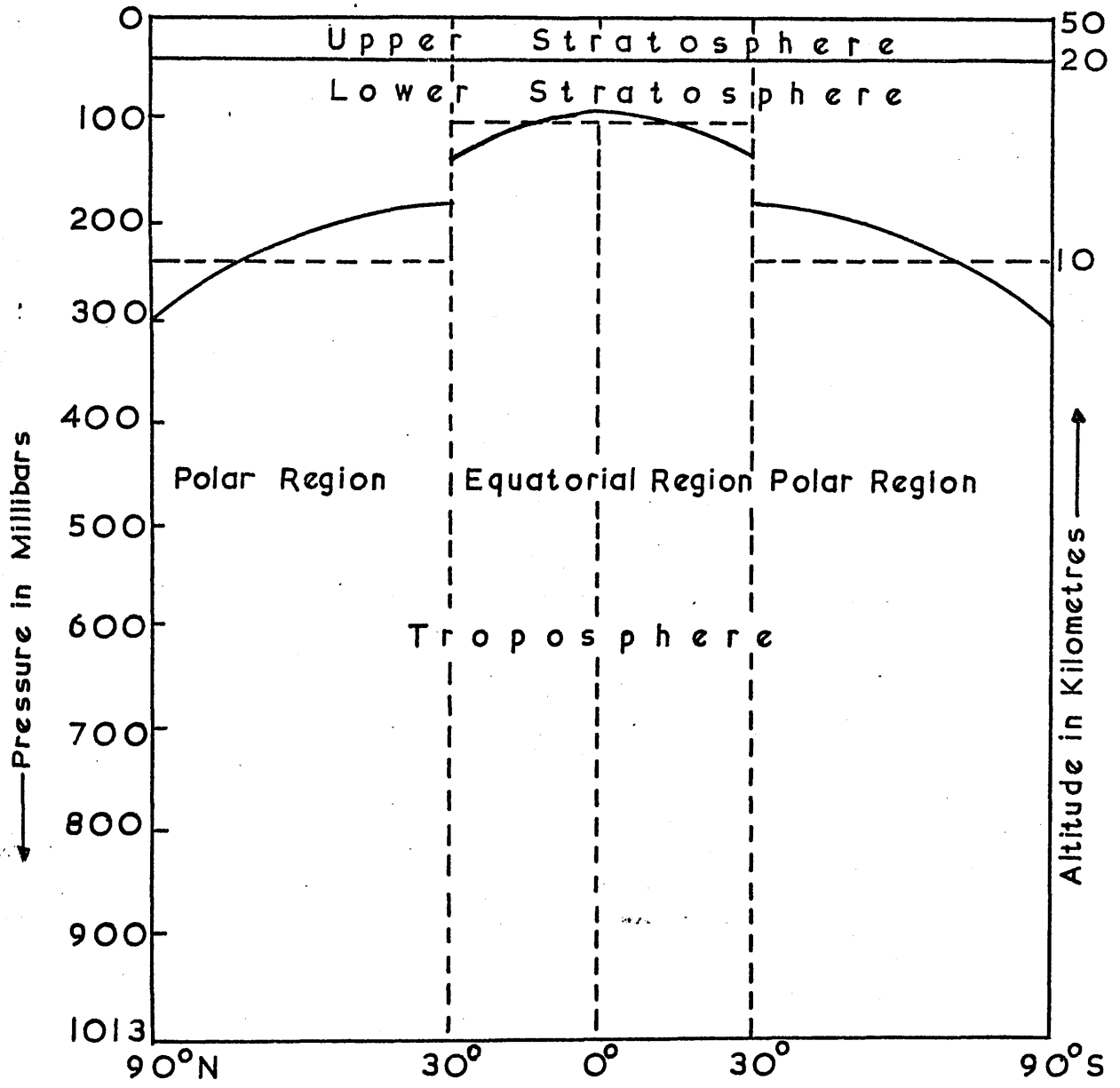
altitude derived from average pressure of the tropopause is 11 km.

The stratosphere extends from the tropopause to about 50 km height - the stratopause. It is generally more stable than the troposphere since convective motions are generally weak or absent. The average temperature is mostly constant, or especially in the upper parts, increasing with height. According to modern workers, Craig (1965) and Goody (1954), the stratosphere should be subdivided into two layers; the lower stratosphere (tropopause to 32 km) and the upper stratosphere (32 km to 50 km).

In calculations the mean height of the tropopause is taken to be 240 mbar in the polar regions and 100 mbar in the equatorial regions. From considerations of available data the lower stratosphere was taken as extending from the tropopause to 40 mbar and the upper stratosphere from 40 mbar to stratopause (Figure 4.13).

As to the oceans, the topmost part above 100 metres is subject to the direct atmospheric influences (layer of surface disturbances) and the water characteristics are homogeneous. Below this region there is a layer with maximum vertical temperature and density gradient. This layer acts as a barrier to vertical motion and mixing, and is termed the thermocline. It tends to be symmetrical about the equator, being moderately thick and quite strong near the equator, becoming thicker, deeper and less intense in the mid-latitudes; and ending at the surface in an intense gradient in the

Figure 4.13. Atmospheric Reservoirs



vicinity of 50° - 60°N and S latitude. It is generally thought to be developed by the equatorward flow of deep cold water from the poles and the poleward flow of warm surface water from the equator (Figure 4.14).

The deep ocean refers to the nearly uniform mass of cold water extending from thermocline to the bottom. Temperature gradients are very weak and it contains about 98% of the total water mass.

In our treatment of the biosphere we have considered this reservoir as comprising all carbon bound in organic structures on land (living material + humus). The mass of organic carbon in the oceans has been disregarded because it is small relative to the large oceanic reservoir of inorganic carbon.

4.2.1. Tropospheric Inventories of Carbon-14

The tropospheric inventories of artificial carbon-14 for July 1967 and July 1968 were calculated in the following manner: The computed carbon-14 concentrations from the above mentioned functions for each month were plotted as a function of latitude (Figures 4.15 and 4.16). Where no carbon-14 data were available for specific latitude bands certain assumptions were made. In the northern hemisphere the carbon-14 concentration was assumed to remain constant above 60°N. This was supported by the carbon-14 data from Nordkapp (71°N) reported by Nydal (1968). In the southern hemisphere the carbon-14 activities were also assumed to remain constant from 0°S to 18°S and above 75°S.

Figure 4.14. Mean Vertical Temperature Distribution in the Oceans and Oceanic Reservoirs

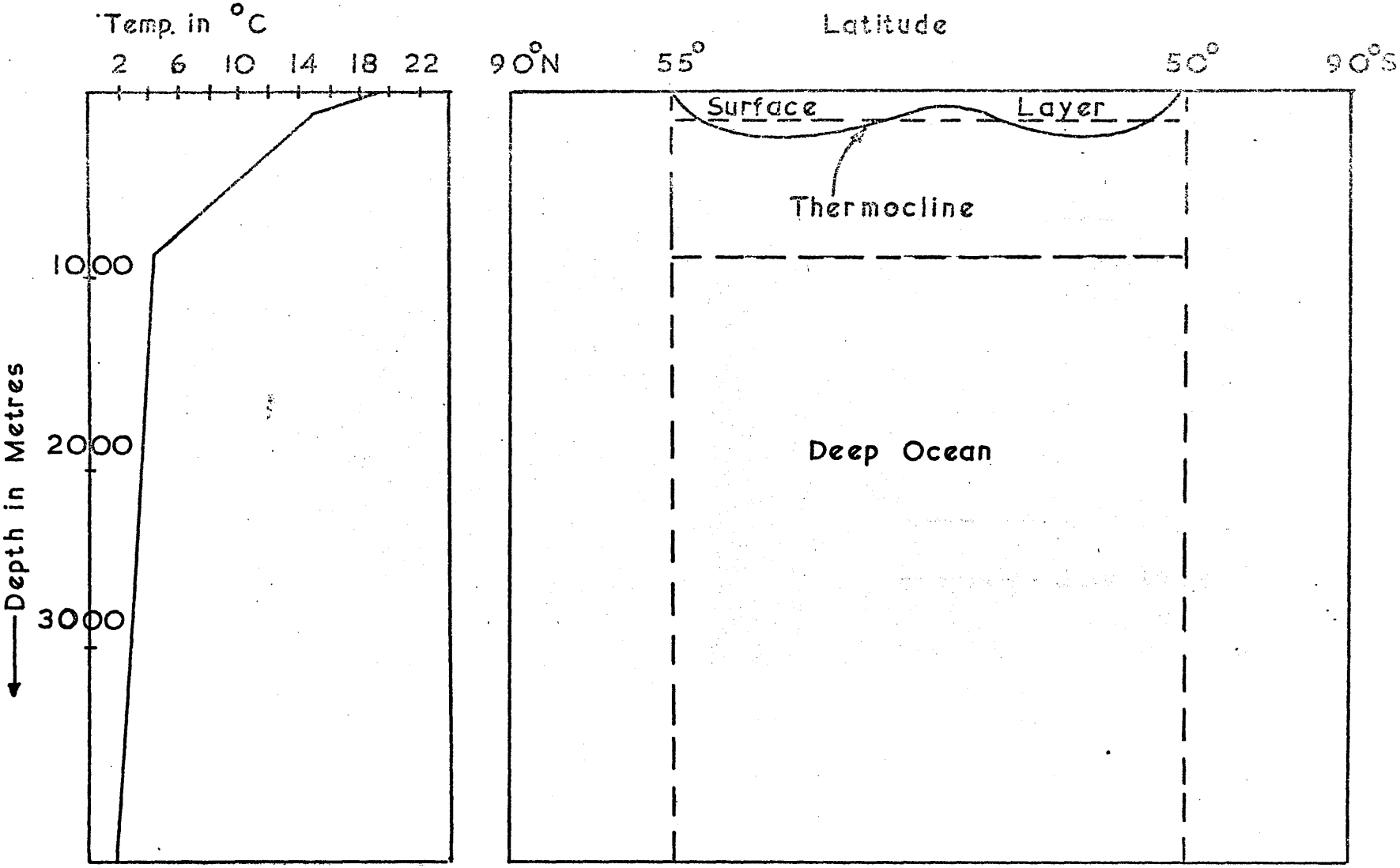


Figure 4.15. Variations of Carbon–14 Concentrations with Latitude in the Northern Hemisphere

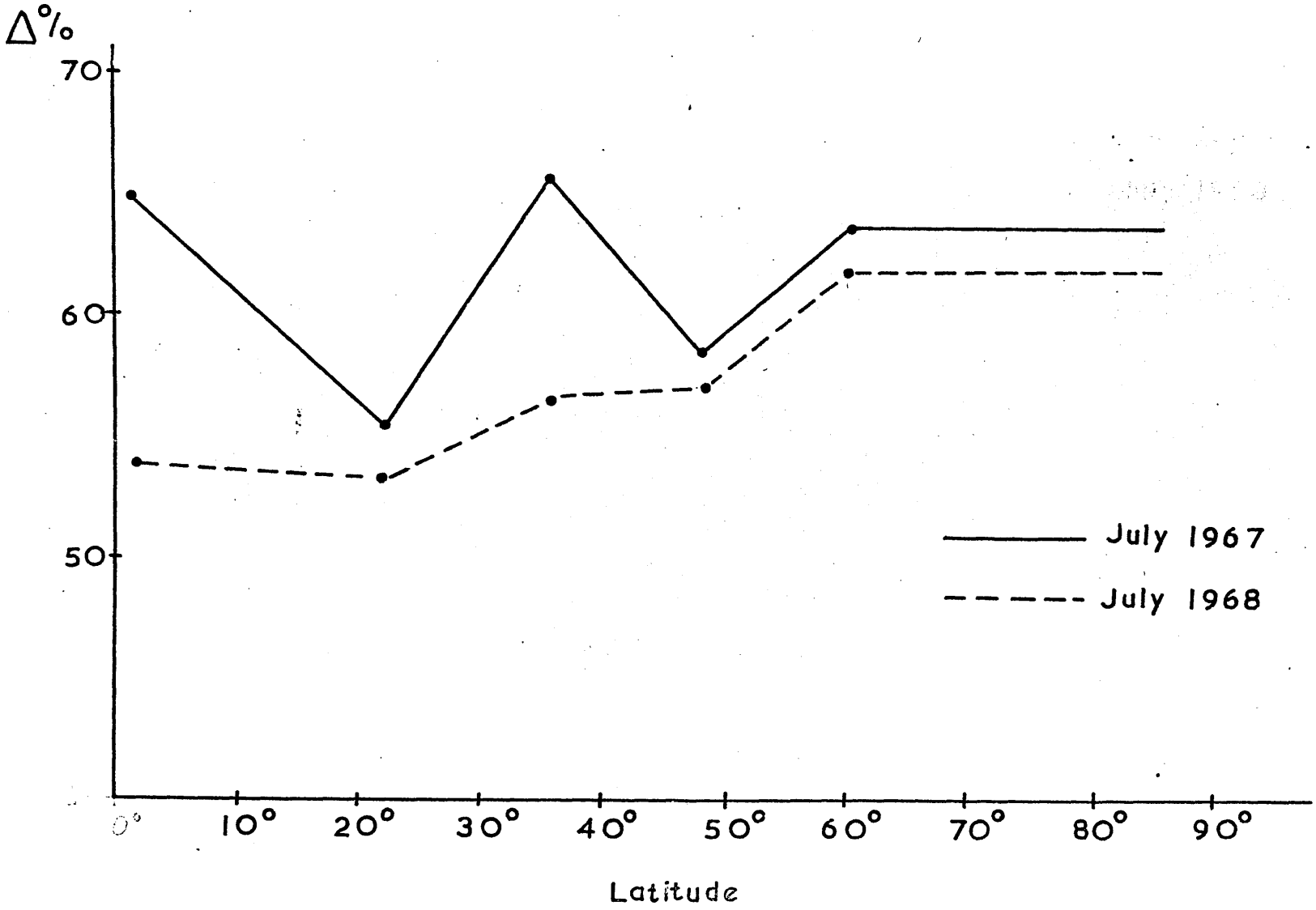
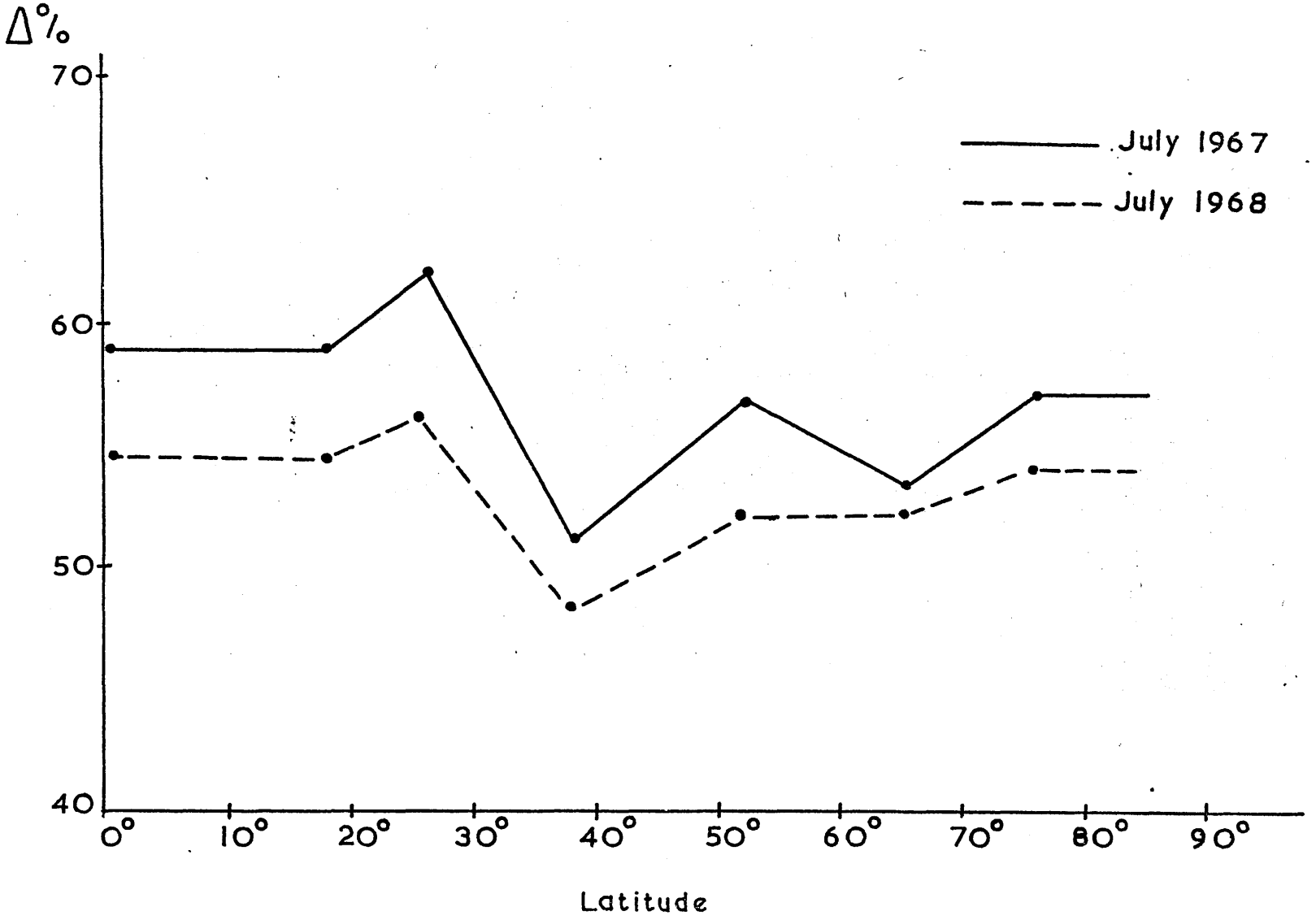


Figure 4.16. Variations of Carbon—14 Concentrations with Latitude in the Southern Hemisphere



An average excess carbon-14 level (Δ) was thus determined for each 10-degree latitude interval by interpolation (Table 4.3). Where significant variations in carbon-14 levels occurred within a 10-degree latitude interval the average value was calculated from smaller interval divisions weighted according to the area of the sector.

The quantity of artificial carbon-14 in each 10-degree latitude band was then calculated from these Δ values, taking into account the mass of tropospheric air in the band and assuming that the troposphere was well mixed vertically. The mass of air in each 10-degree latitude interval was calculated from the relationship

$$M = \frac{P - P_t}{g} \times 10^3 \times A \times 0.5 \left(\sin \bar{\Phi}_2 \overset{\sin}{-\lambda} \bar{\Phi}_1\right)$$

where, M = The mass of air in any tropospheric box bounded by latitude bonds $\bar{\Phi}_1$ and $\bar{\Phi}_2$.

P = Atmospheric pressure at sea level (1013.25 mbar).

P_t = Pressure at tropopause.

g = 980.6 cm/sec^2.

A = Surface area of the earth.

The results are shown in Table 4.4.

In the inventory calculations the current "Suess effect" was taken into account as follows. Recent work by Baxter (1969), suggests that the magnitude of this effect is -5.34% in the atmosphere at the beginning of 1967 and -5.53% at the beginning of 1968. The size of the effect in the surface

Table 4.3. Tropospheric carbon-14 concentrations (1967-68)

Latitude band	July 1967*		July 1968*	
	N. Hemisphere	S. Hemisphere	N. Hemisphere	S. Hemisphere
0° - 10°	63.00	58.89	53.50	54.35
10° - 20°	58.60	58.96	53.30	54.40
20° - 30°	58.00	60.40	53.60	54.90
30° - 40°	65.60	53.95	56.10	50.35
40° - 50°	61.40	53.75	57.00	50.00
50° - 60°	61.00	55.85	59.50	52.04
60° - 70°	63.54	53.95	61.81	52.38
70° - 80°	63.54	56.65	61.81	53.65
80° - 90°	63.54	57.25	61.81	54.20

* Δ - Per cent

Table 4.4. Quantity of artificial carbon-14 in the troposphere (10^{25} atoms)

Latitude band	In July 1967		In July 1968	
	N. Hemisphere	S. Hemisphere	N. Hemisphere	S. Hemisphere
0° - 10°	191.79	179.28	162.87	165.46
10° - 20°	172.55	173.61	156.94	160.18
20° - 30°	159.79	166.40	147.67	151.25
30° - 40°	157.48	129.51	134.67	120.87
40° - 50°	121.00	105.92	112.33	98.53
50° - 60°	93.17	85.30	90.88	79.48
60° - 70°	69.17	58.73	67.28	57.02
70° - 80°	41.75	37.23	40.62	35.25
80° - 90°	14.01	12.62	13.63	11.95
Total	1020.71	948.60	926.89	879.99

oceans is estimated to be -3.10% in 1967 and -3.21% in 1968. These values were calculated on a predicted 3.5% average annual increase in fossil fuel consumption throughout the world.

The tropospheric inventory was therefore calculated from the values corrected for the Suess effects given above. It was found that the quantity of artificial carbon-14 in the troposphere was 21.03 x 10^{27} atoms in July 1967 and 20.04 x 10^{27} atoms in July 1968.

4.2.2. Stratospheric Inventories of Carbon-14

Due to lack of data, the stratospheric carbon-14 inventories for 1967 and 1968 were derived by extrapolation of the previous years' results.

Recently, Harkness (1969) re-evaluated the stratospheric carbon-14 data (as published by the U.S.A.E.C. Health and Safety Laboratory) using a more refined technique. According to his treatment the stratosphere could not be considered as a single unit since it was not well mixed vertically during 1967-1968; and therefore, must be subdivided into upper and lower regions. In order to derive the inventory it was assumed that the carbon-14 concentration at mid-altitude (in terms of mass) is representative of the whole of the stratospheric region under study.

For the upper stratosphere (40 mbar - stratopause) the physical mid-altitude is 20 mbar and an exponential decrease of concentrations with time has been assumed. The following

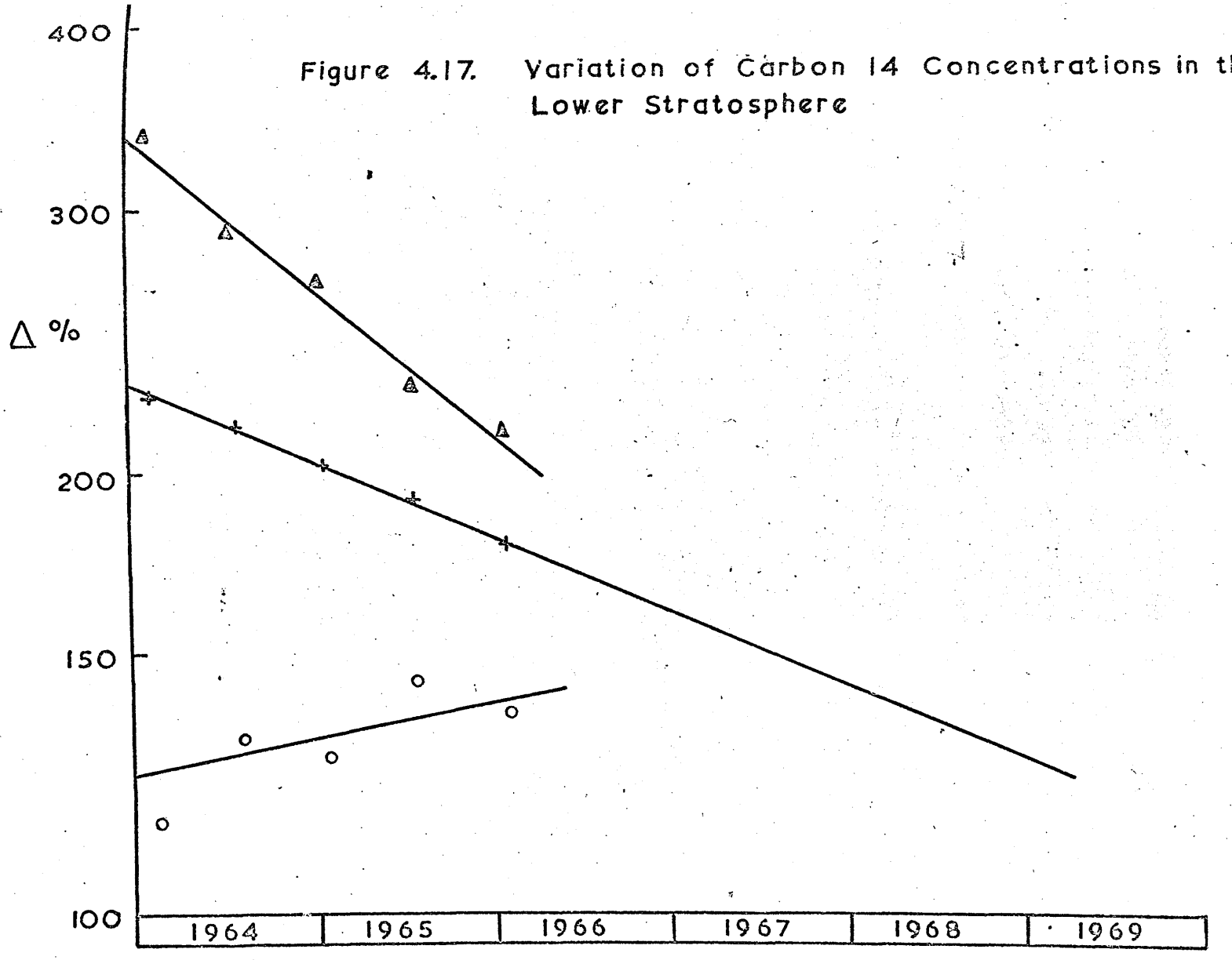
function describes the behaviour of carbon-14 concentrations in the upper stratosphere and was found by applying the least mean-squares method to the observed data of 1963-65 (See Appendix C).

$$y = 878\ e^{-0.0365t}$$

where t denotes time, t = 0 for 1st February 1963, and y denotes the excess carbon-14 (Δ). From this function the Δ values for July 1967 and July 1968 were calculated to be 319‰ and 256‰ respectively, corrected for the Suess effect. These values were then converted to the number of atoms of carbon-14, assuming the background level to be 13.1 dpm $^{14}C/g$ carbon and the mass of the total carbon in the reservoir to be 2.47×10^{16} g. From these assumptions it has been calculated that the upper stratosphere contained about 10.48×10^{17} dpm ^{14}C and 8.45×10^{17} dpm ^{14}C corresponding to 4.4×10^{27} atoms and 3.6×10^{27} atoms of artificial carbon-14 in July 1967 and July 1968 respectively.

For the lower stratosphere (tropopause - 40 mbar), the mean carbon-14 concentrations for the sections 30° - 90°N, 0° - 30°N and 0° - 90°S were determined in the same manner as for the total upper stratosphere, using the data collected during 1964 through 1965. An overall negative gradient was noted for the northern hemisphere and a positive gradient was noted for the southern hemisphere. The extrapolation of these curves showed that in the lower stratosphere homogeneity between the hemispheres occurred during early 1967 (Figure 4.17). Therefore, to obtain representative values after this time a plot of the decrease in the total lower stratospheric carbon-14

Figure 4.17. Variation of Carbon 14 Concentrations in the Lower Stratosphere



content was prepared up to 1967, and this line extrapolated through 1968 as shown in Figure 4.17. This curve is represented by the following function:

$$y = 227.4\ e^{-0.1288t}$$

where y denotes the excess carbon-14 (Δ) and t denotes time, t = 0 for 1st February 1964. According to this function the carbon-14 concentrations (Δ) were 144‰ in July 1967 and 127.3‰ in July 1968. It was again assumed that the natural level was 13.1 dpm $^{14}C/g$ carbon, the total carbon in the reservoir 8.03×10^{16} g and the Suess effect -5‰. With these values the artificial carbon-14 in the lower stratosphere has been calculated to be 15.67×10^{17} dpm ^{14}C in July 1967 and 13.92×10^{17} dpm ^{14}C in July 1968, corresponding to 6.6×10^{27} atoms ^{14}C and 5.9×10^{27} atoms ^{14}C respectively.

4.2.3. Biospheric Inventories of Carbon-14

The amount of artificial carbon-14 in the biosphere cannot be accurately determined by direct measurement because of the difficulty in obtaining representative samples. We have calculated the excess carbon-14 in the biosphere (terrestrial + humus) in the following manner.

Estimates of the size of the land biosphere vary considerably but recent reviews of the data by Leith (1963) and Junge and Czeplak (1967) indicate that the most likely values for the amount of carbon in the biosphere (terrestrial + humus) and the rate of fixation of atmospheric carbon are

8.34×10^{17} g and 0.384×10^{17} g/year respectively. Thus the cycling time of a carbon atom in the biosphere is $8.34/0.384 = 22$ years.

It has been reported by Walton et al (1967) that the carbon-14 activity measurements of plant materials give results identical with those obtained for contemporary tropospheric air. Therefore, assuming that no mixing of fixed carbon occurs within the reservoir, the mean excess carbon-14 concentration in any year n can be calculated from the following relationship:

$$\Delta'_n = \frac{m}{M} \left(\Delta_n + \Delta_{n-1} + \Delta_{n-2} + \cdots\cdots + \Delta_{n-22}\right)$$

where, Δ' = mean biospheric excess carbon-14 level.

Δ = mean tropospheric excess carbon-14 level.

m = ~~annual fixation rate (g/year)~~ g carbon fixed in one year in the biosphere.

M = total carbon in the biosphere (g).

Due to the considerable variations in carbon-14 concentrations throughout the troposphere during the period of 1955-1968 the total biosphere was treated on an hemispheric basis. The mass of biosphere was divided relative to the annual fixation rates of 0.226 g/year and 0.158 g/year in the northern and southern hemispheres respectively. Calculations were then made using the tropospheric data for the growth period in both hemispheres for each year and the results from 1959 to 1968 are shown in Table 4.5. As seen in Table 4.5 the average excess carbon-14 levels were 18.97% in July 1967 and 21.50%

Table 4.5. Biospheric carbon-14 ($\Delta^{14}C$) concentrations (1959-1968)

Year	N. Hemisphere	S. Hemisphere	Mean (weighted)
1959	-0.28	-0.64	-0.42
1960	0.83	0.28	0.62
1961	1.84	1.20	1.58
1962	3.32	2.16	2.85
1963	6.72	4.00	5.60
1964	11.50	6.76	9.52
1965	15.30	9.80	13.04
1966	18.40	12.70	16.03
1967	21.40	15.50	18.97
1968	24.00	18.00	21.50

in July 1968. The natural level was assumed to be 13.1 dpm $^{14}C/g$ carbon (the same as the atmospheric level). With these assumptions the artificial carbon-14 in the biosphere has been calculated to be 23.99×10^{17} dpm ^{14}C in July 1967 and 26.84×10^{17} dpm ^{14}C in July 1968, corresponding to 10.1×10^{27} atoms ^{14}C and 11.3×10^{27} atoms ^{14}C respectively.

4.2.4. Inventories of Carbon-14 in the Oceans

The inventory calculations for the surface layers of the ocean have been based on the measurements of Nydal (1967, 1968), Rafter (1968) and Young and Fairhall (1968). About 60 results were obtained, mainly from the Atlantic and Pacific oceans, for the period 1967-1968. Almost half of these data were obtained in the southern hemisphere. The results scattered over a range of Δ from + 4% to + 27% indicating considerable inhomogeneity in carbon-14 concentrations in the surface water of the oceans. The general trend was such that the total excess carbon-14 appeared to increase with time. In order to evaluate the inventory of artificial carbon-14, a mean concentration was found by averaging the present data for each month for the northern and southern hemisphere separately and then an average of the monthly mean values was calculated to obtain a yearly mean carbon-14 concentration. This was performed for 1967 and 1968, and the average Δ values of +9.92% and +10.62% determined. These values were considered to be representative for the middle of the corresponding years. Assuming the Suess

effect is -3% in the surface ocean, the actual number of artificial carbon-14 atoms contributed by weapons tests are equivalent to increases of 12.92% and 13.62% above the natural level. We assumed further that the amount of total carbon in the surface layer is 8.16×10^{17} g. With these assumptions the average total excess carbon-14 activities in the surface layer of the oceans has been calculated to be 13.81×10^{17} dpm ^{14}C in July 1967 and 14.56×10^{17} dpm ^{14}C in July 1968, corresponding to 6.1×10^{27} atoms and 6.4×10^{27} atoms carbon-14 respectively.

To summarize, we have found that in July 1967 there were 46.9×10^{27} atoms of artificial carbon-14 and in July 1968 45.4×10^{27} atoms, distributed in the various reservoirs as shown in Table 4.6. Some of the difference between these two results can be accounted for by transfer of carbon-14 to the deep oceans. It must be borne in mind, however, that these figures are subject to considerable uncertainties in the average carbon-14 concentrations assessed for the reservoirs.

The accuracy of these results varies from reservoir to reservoir. For the stratosphere and the troposphere neither the measurements of carbon-14 concentrations, nor the masses of air in these reservoirs are subject to large uncertainty, and the accuracy is believed to be better than ±10%. For the biosphere and ocean surface layer a considerable error, possibly a factor of two, may be involved, due to the uncertainty in the reservoir sizes and carbon-14 measurements. For example,

Table 4.6. Distribution of artificial carbon-14 in the carbon cycle (x 10^{27} atoms)

		July 1967	July 1968
Stratosphere	upper:	4.4	3.6
	lower:	6.6	5.9
Troposphere:		19.7	18.2
Biosphere (terr. + humus):		10.1	11.3
Ocean surface layer:		6.1	6.4
Total		46.9	45.4

the scatter of the results of the ocean surface was large, the calculated standard deviation was about ± 40% of the average value. However, the total inventory of excess carbon-14 is in reasonable agreement with the inventories of 54 x 10^{27} atoms, estimated by Young and Fairhall (1968) and 57 x 10^{27} atoms, calculated by Walton et al (1964, unpublished) for earlier times.

The total yield of weapon tests announced up to and including 1962 was 406 Mton from air bursts, and 105 Mton from surface bursts (Table 4.1). On the basis of these yields and the estimated release of neutrons per Mton (2 x 10^{26} n/Mton in the case of an air burst, 1 x 10^{26} n/Mton for a surface burst) it has been calculated that the total production of carbon-14 was 92 x 10^{27} atoms. The total carbon-14 which has been produced, mainly by the Chinese and French tests of June 1967 and July 1968, since 1963 is approximately 3 x 10^{27} atoms. The contribution from these latter tests in our data is probably negligible since the excess carbon-14 values of the stratosphere to date were found by extrapolation from the results available until 1966. The difference between 92 x 10^{27} atoms and the result presented here may be explained by the magnitude of errors on the basic assumptions which were made for calculations in both cases, viz., neutron yields, Δ values in the surface ocean layers, and the treatment of the biosphere.

CHAPTER 5. CALCULATION OF CO_2 EXCHANGE TIMES IN THE CARBON CYCLE FROM THE DISTRIBUTION OF ARTIFICIAL CARBON-14 IN 1967-1968

One of the fundamental assumptions of the radiocarbon dating method is that the carbon-14 concentration in the atmosphere has been essentially constant with time, i.e., the removal of carbon-14 is balanced by the production of carbon-14 by cosmic rays. This steady-state situation has been modified during the last 100 years by the Industrial effect and, over the last 20 years by the testing of nuclear weapons. The study of the carbon-14 steady-state situation and the above transient disturbances of that steady state in nature are of assistance in elucidating the various exchange rate constants for CO_2 in the carbon cycle.

First measurements of the decrease in carbon-14 specific activity of the atmosphere and the contemporary portion of the biosphere owing to the release of substantial quantities of carbon-14 free carbon dioxide by combustion of fossil fuels were made by Suess (1953, 1955). By considering the magnitude of the industrial effect and the steady-state distribution of carbon-14 in the atmosphere and oceans, Revelle and Suess (1957) and Arnold and Anderson (1957) estimated that the CO_2 exchange time between the atmosphere and the ocean must lie between one and two decades. From further measurements on the world-wide

industrial effect, Fergusson (1958) has estimated that the above-mentioned exchange time must be less than seven years and is probably of the order of two years.

The values of the above exchange times are of considerable importance and hence they have been supplemented by calculations using bomb-produced carbon-14 as a tracer, Lal and Rama (1966), Bien and Suess (1967), Young and Fairhall (1968) and Nydal (1968). Considerable disagreement still exists in the available data. Therefore a continued study of environmental carbon-14 levels appears necessary to permit further, and hopefully, more accurate assessments of the CO_2 transport parameters between the various reservoirs of the carbon cycle.

To evaluate the exchange rates between various reservoirs a box-model approach has been adopted. The atmosphere - ocean system has been divided into a series of independent reservoirs and the transfer of carbon between reservoirs was assumed to be determined by first order rate constants. For the biosphere and the surface oceans the actual circumstances depart from these idealised situations. In the case of the biosphere there will be some uncertainty due to the hold-up of biospheric carbon-14 in humus before transfer back to the atmosphere, and in the case of the surface ocean uncertainty will arise because of the variable rate of mixing with deep ocean water at different latitudes.

5.1. Application of Carbon-14 Data to Box Models

One of the basic difficulties in applying a box model treat-

ment to the study of carbon exchange in nature is the meaningful interpretation and application of environmental carbon-14 levels. Any box model representation implies ideal conditions which clearly do not exist in the natural environment. These conditions include the assumption of uniform concentration for the carbon-14 tracer within a particular box, and a uniform transfer flux for carbon across the boundaries between adjacent boxes. To overcome these limitations it is necessary to equate measured values in terms of the conditions defined by the model. Where inhomogeneity of carbon-14 concentrations exist it is necessary to calculate either the mean carbon-14 level for the whole box or consider a particular representative region. In the case of time variations in mass transfer which can arise in cyclic seasonal effects these may be overcome by assuming a mean variation for the whole year or by comparison of carbon-14 values for identical times in separate years.

An important aspect of model construction is the selection of boundaries. In many cases these may be more apparent than real, being convenient divisions for consideration of measured data rather than actual physical barriers to carbon transport. Many natural interfaces, however, are obvious, viz., the tropopause, the ocean thermocline, although even these are by no means accurately defined.

In spite of all the necessary approximations to be made in the application of box models, it appears to be the best method of calculation of the exchange rates between various dynamic carbon reservoirs at the present time.

5.2. Definition of Residence and Exchange Times

Due to the different interpretations which have appeared in the literature regarding the concept of residence time a complete definition is given here.

The residence time, τ , is defined as the average life of a CO_2 molecule in a reservoir before it is transferred to another reservoir. It is the time required for an original number, N_o, of particular molecules to be reduced to 1/e of the initial number and is thus mathematically equivalent to a radioactive mean life. Therefore the change in number of the molecules, dN, in one reservoir in the time interval dt can be expressed by the relationship

$$\frac{dN}{dt} = - kN$$

by integration $$N = N_o e^{-kt}$$

since $$N = \frac{N_o}{e}, \quad \frac{1}{e} = e^{-kt}$$

therefore $$t\ (\tau) = \frac{1}{k}$$

where k is the exchange rate constant.

In case of several adjacent reservoirs the mean residence time in one reservoir is dependent on the separate residence times with respect to each of the other reservoirs. In order to avoid confusion the residence time (τ) with respect to one

of the adjacent reservoirs will be called "the exchange time" and it will be defined as the reciprocal of the exchange rate constant, $1/k$.

The exchange time and the residence time are identical when the exchange takes place only between two reservoirs. Where a number of adjacent reservoirs exist the mean residence time can be expressed as follows:

$$\frac{1}{\tau} = \frac{1}{\tau_1} + \frac{1}{\tau_2} + \cdots\cdots + \frac{1}{\tau_n}$$

where τ_1, τ_2, ... , τ_n are the exchange times.

In terms of exchange rate constants the relationship is

$$k = k_1 + k_2 + \cdots + k_n$$

5.3. Calculation of Exchange Times

In each model the main body of the atmosphere has been divided into two well mixed reservoirs, namely, the stratosphere and the troposphere. In the same way the ocean is divided into a well mixed surface reservoir, depth taken as 100 metres (often referred to as the "surface layer") and a much larger deep reservoir. In each reservoir the exchange times of CO_2 with respect to adjacent reservoirs have been calculated.

The method of calculation of exchange times makes use of the equations applicable to the steady-state distribution for natural carbon. It is further assumed that carbon-14 behaves in a similar manner to carbon-12. Thus the relative rates of

change for excess carbon-14 concentrations in various reservoirs are governed by the interreservoir exchange rates of all carbon.

In the following sections the assumptions, calculations and results are discussed for four models which are believed to be most representative of the physical situation within the limitations described previously.

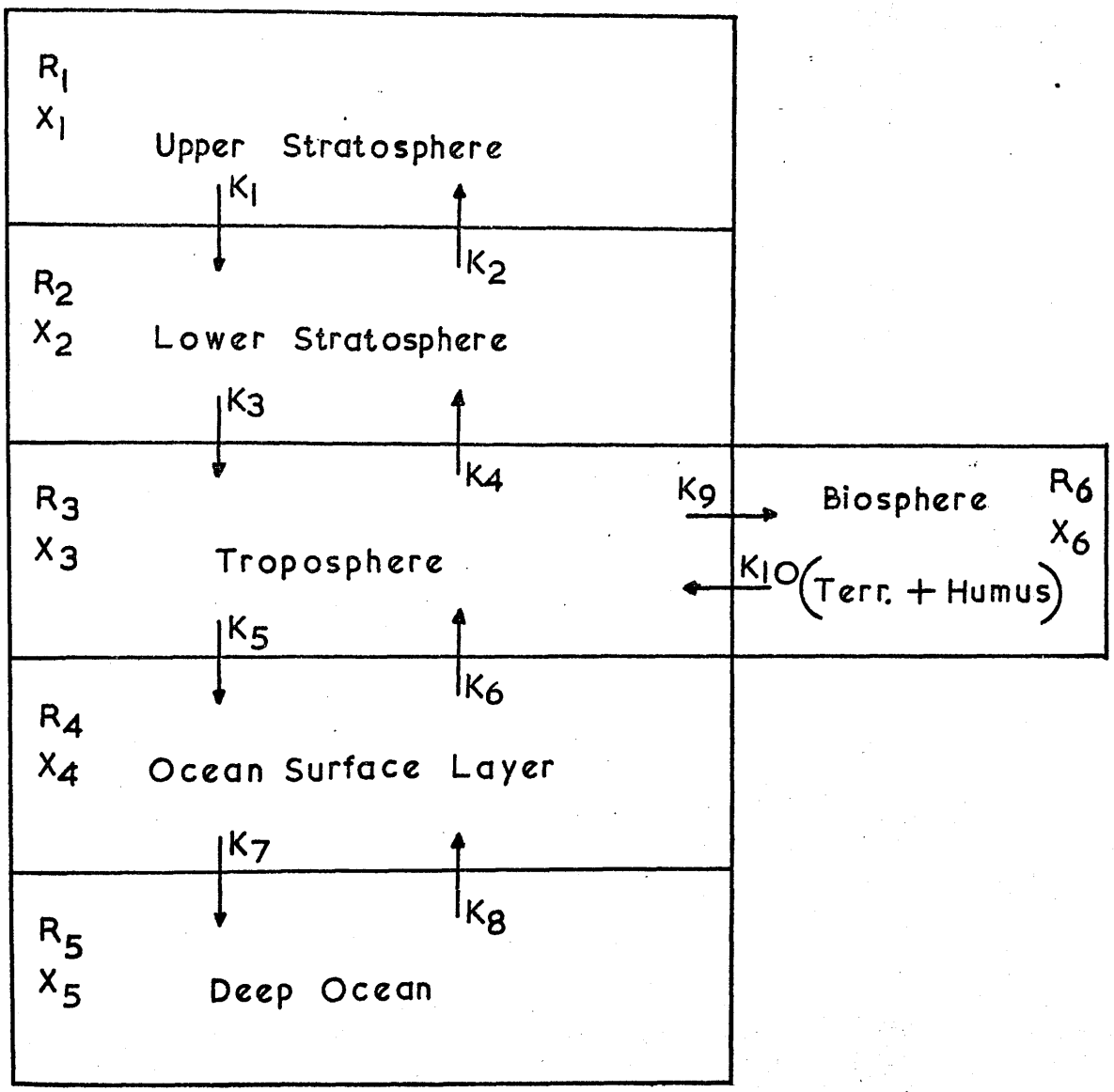
5.3.1. Model 1; assumptions, calculations and results

This model consists of six boxes as shown in Figure 5.1. The atmosphere is subdivided into troposphere, the lower stratosphere and the upper stratosphere. The ocean is subdivided into the surface layer and the deep ocean. The boundaries between the reservoirs are as described in the previous chapter. The biosphere (terrestrial + humus) is considered as one box in exchange only with the troposphere. These reservoirs are assumed to be in steady-state with respect to CO_2 transport and distribution and it is further assumed that exchange occurs according to first-order kinetic processes. Using these assumptions the time-dependent rate of exchange of excess carbon-14 in the various boxes can be represented by the following series of simultaneous equations:

$$R_1 \frac{dx_1}{dt} = R_2 x_2 k_2 - R_1 x_1 k_1$$

$$R_2 \frac{dx_2}{dt} = R_1 x_1 k_1 + R_3 x_3 k_4 - R_2 x_2 k_2 - R_2 x_2 k_3$$

Figure 5.1. Model 1.



$$R_3 \frac{dx_3}{dt} = R_2 x_2 k_3 + R_4 x_4 k_6 + R_6 x_6 k_{10} - R_3 x_3 k_4 - R_3 x_3 k_5 - R_3 x_3 k_9$$

$$R_4 \frac{dx_4}{dt} = R_3 x_3 k_5 + R_5 x_5 k_8 - R_4 x_4 k_6 - R_4 x_4 k_7$$

$$R_6 \frac{dx_6}{dt} = R_3 x_3 k_9 - R_6 x_6 k_{10}$$

where R_i represents the mass of total carbon and x_i represents the percentage of excess carbon-14 concentration in box i. k_i represents the exchange rate constant from box i to an adjacent box, which is to be determined. dx_i/dt is the rate of change of carbon-14 concentrations in box i. The exchange rate constants k_1 and k_2 are related by the identity $k_1 R_1 = k_2 R_2$, as required for conservation of masses within the reservoirs, upper and lower stratospheres. Similarly, $k_3 R_2 = k_4 R_3$, $k_5 R_3 = k_6 R_4$, $k_7 R_4 = k_8 R_5$ and $k_9 R_3 = k_{10} R_6$. The values of the parameters applied are shown in Table 5.1

R_1, R_2 and R_3 were calculated from the total atmospheric inventory of carbon given by Takahashi (1967) and the available data on mean tropopause heights, the 40 mbar boundary between the lower and upper stratospheres and the stratopause height. R_4 and R_5 were taken as calculated by Broecker and Olson (1960). R_6 was found by summing up the terrestrial carbon, 1.09×10^{17} g, and humus, 7.25×10^{17} g, as determined by Leith (1963). Since the values of x_i and dx_i/dt vary with time they were determined

Table 5.1. Parameters applied in Model 1

Reservoir	Reservoir size (R) $\times 10^{17}$ g carbon	Excess ^{14}C (x) ‰	Gradient (dx/dt) ‰ per year
Upper stratosphere	0.247	256.0	-56.1
Lower stratosphere	0.803	127.3	-16.4
Troposphere	5.52	54.9	-4.8
Surface Ocean	8.16	10.6	0.7
Deep Ocean	371.0	-17.6	-
Biosphere	8.34	21.5	3.26

for a fixed time, July 1968 in order to avoid any mistake which may be introduced by seasonal variations. x_1 and x_2 were determined by extrapolation of previous years' results which were evaluated by Harkness (1969) as mentioned earlier. x_3 was determined from measurements, performed by the author, of tropospheric carbon-14 concentrations by plotting the excess carbon-14 concentrations as a function of time (Figure 5.2). The determination of x_4 was based on the measurements of the carbon-14 concentrations in the surface water of mainly Atlantic and Pacific oceans. Again the excess carbon-14 concentrations, measured by Nydal (1969), Rafter (1968) and Young and Fairhall (1968), were plotted as a function of time and the value of x_4 obtained from the curve (Figure 5.3). x_5 was obtained by averaging (weighted) the values for Atlantic and Pacific deep water given by Broecker and Olson (1960) and Bien and Suess (1967) respectively. The deep ocean results were taken as measured by the above mentioned authors several years ago. Because of the size of this reservoir (about 60 times of the atmospheric reservoir) the increase in average carbon-14 concentration in the deep ocean would not be at a detectable level in 1968.

It was difficult to assign a value to x_6, the biospheric carbon-14 concentration, since there were no measured representative values. It was calculated, therefore, from the reservoir size (8.34×10^{17} g) and annual fixation rate (0.384×10^{17} g) of carbon, and assuming that the carbon-14 activities of plant

Figure 5.2. Variation of Excess Carbon—14 Concentrations in the Troposphere

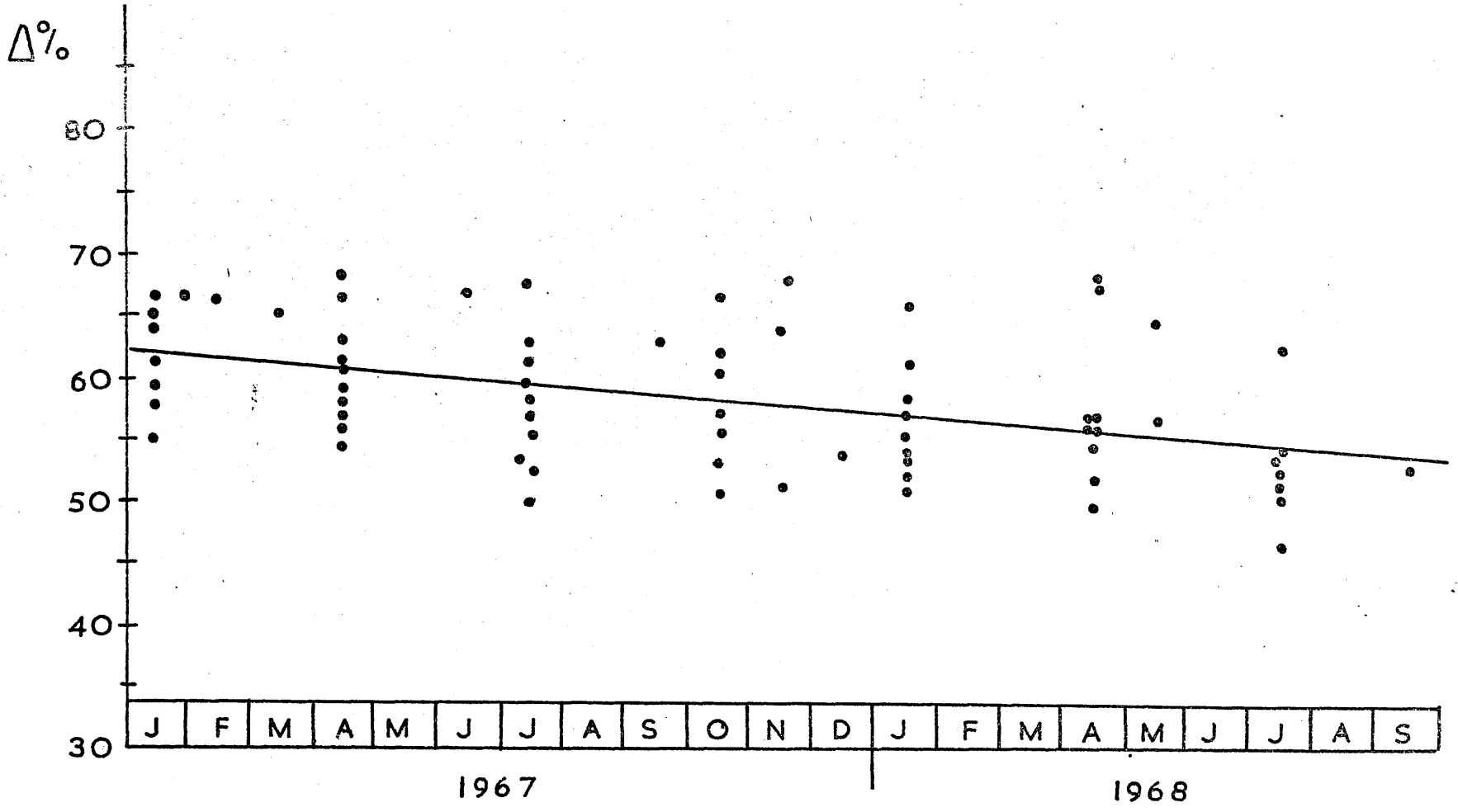
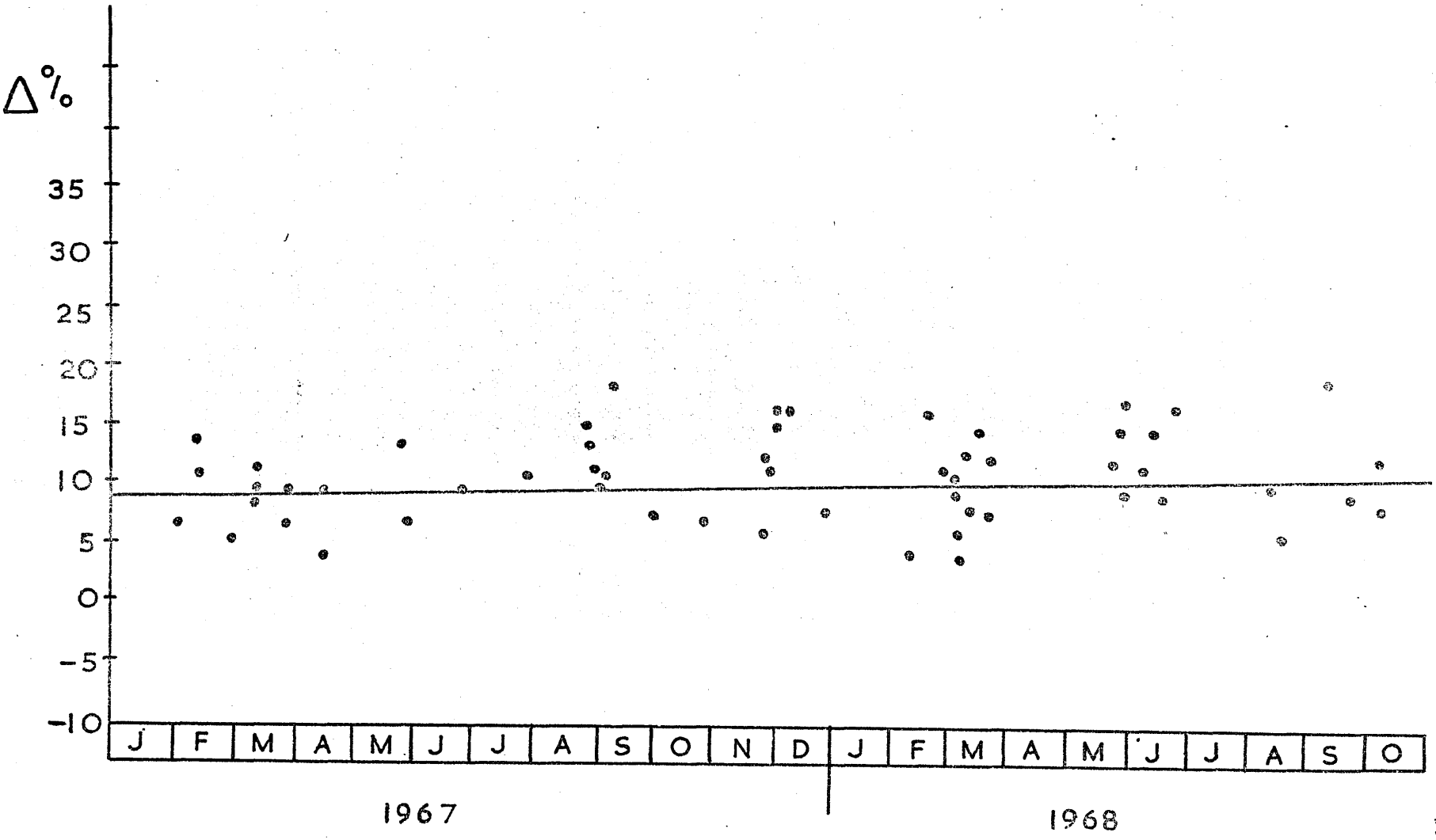


Figure 5.3. Variation of Excess Carbon–14 Concentrations in the Ocean Surface Water



material are identical with those for contemporary tropospheric air and that no mixing of fixed carbon occurs within the reservoir.

The values of dx_i/dt were determined by differentiating the functions which represent the change of excess carbon-14 concentration with time in each box. These functions were found from the observed, or in the case of the biosphere from the calculated values by computer analysis. The following functions were used for the various reservoirs:

Upper stratosphere: $x = 878e^{-0.0365t}$, $t = 0$ for 1st February 1963

Lower stratosphere: $x = 227.4e^{-0.1288t}$, $t = 0$ for 1st February 1964

Troposphere: $x = -4.8t + 62.5$, $t = 0$ for 1st January 1967

Surface ocean: $x = 0.057t + 9.5$, $t = 0$ for 1st January 1967

Biosphere: $x = 12.6e^{0.1516t}$, $t = 0$ for 1st July 1964

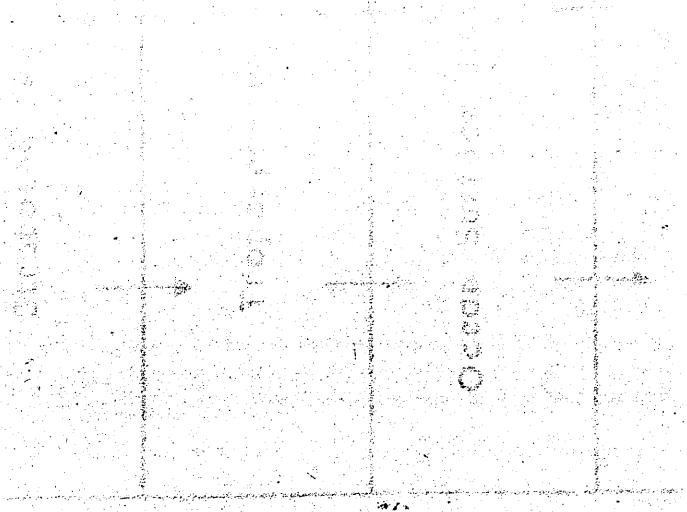
From the relations for conservation of masses within the boxes the values of k_2, k_4, k_6, k_8 and k_{10} can be expressed in terms of k_1, k_3, k_5, k_7 and k_9 respectively. Substituting them in the above equations and solving these five simultaneous equations gave the exchange times shown in Table 5.2.

5.3.2. Model 2, (5 boxes)

This model is a simplified form of Model 1 (Figure 5.4). The stratospheric boxes were combined and the total stratosphere has been represented as a single box. R_1, the total carbon

Table 5.2. Exchange times calculated from Model 1

Reservoirs in exchange	Exchange time (τ, year)
Upper-Lower Stratosphere	2.3
Lower Stratosphere - Troposphere	2.1
Troposphere - Surface Ocean	9.3
Troposphere - Biosphere	6.8
Surface - Deep Ocean	11.2
Deep - Surface Ocean	508



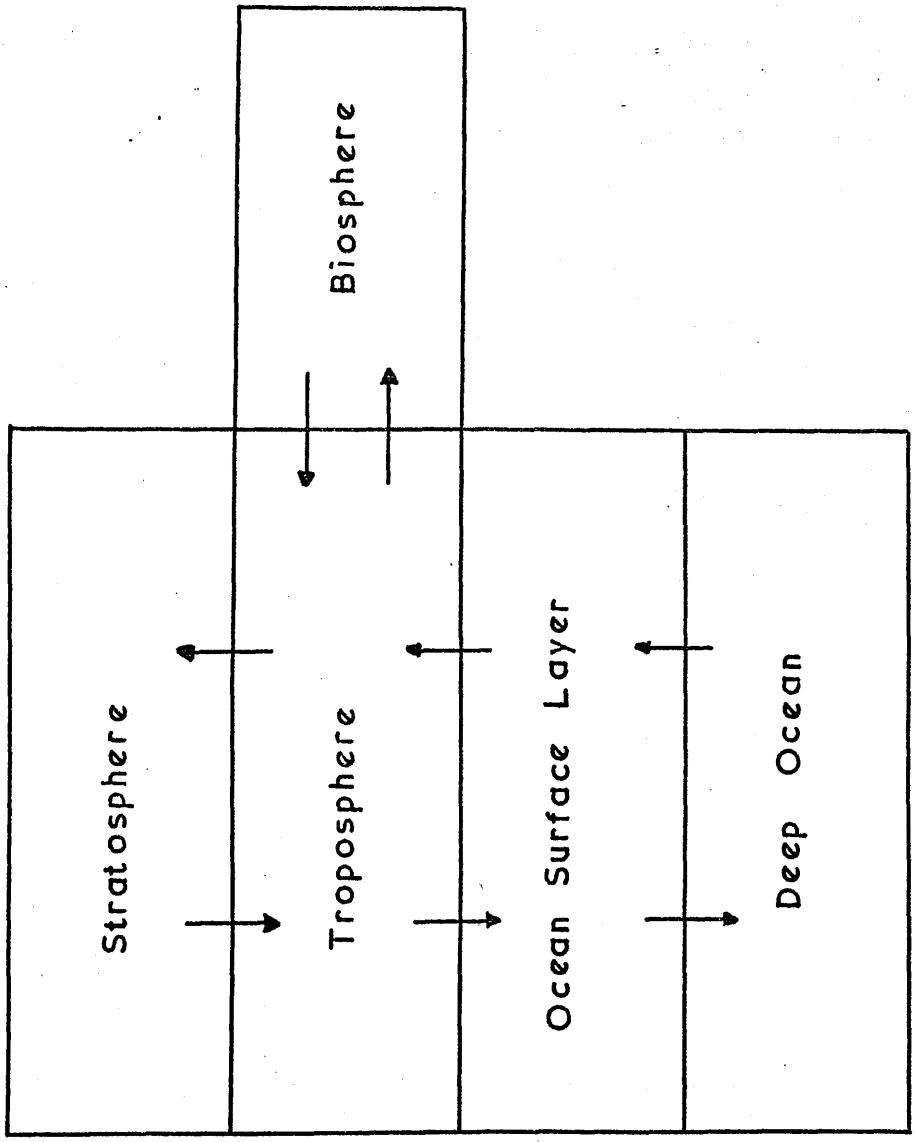


Figure 5.4. Model 2.

in the stratosphere, was taken as 1.05×10^{17} g (sum of R_1 and R_2 in the Model 1). x_1 and dx_1/dt were taken to be 157.6% and -25.7%/year respectively (weighted mean values of the upper and lower stratospheric values). The exchange times were calculated using the same method as Model 1 and the parameters shown in Table 5.3. The results are shown in Table 5.4.

5.3.3. Model 3, (8 Boxes)

This model is similar to Model 2 (Figure 5.5). The major difference is that the troposphere, the ocean surface layer and the biosphere were subdivided into two boxes through the equator. The tropospheric reservoirs were assumed to be symmetric across the equator with regard to size and exchange rate constants. The ocean surface layer and the biospheric reservoirs, however, were treated as being asymmetric. The ocean surface layer was divided into two according to the surface areas in each hemisphere, and the biosphere was divided according to the annual fixation rates of carbon in the northern (22.6×10^{15} g) and southern (15.8×10^{15} g) hemispheres. Due to absence of a measurable meridional gradient within the box (complete horizontal homogeneity was attained by early 1967) no attempt has been made to subdivide the stratospheric reservoir.

To aid the solution of the equations generated in this model it was assumed that the CO_2 exchange between the surface

Table 5.3. Parameters applied in Model 2

Reservoir	Reservoir size (R) x 10^{17} g carbon	Excess ^{14}C (x) %	Gradient (dx/dt) % per year
Stratosphere	1.05	157.6	-25.7
Troposphere	5.52	54.9	-4.8
Surface Ocean	8.16	10.6	0.7
Deep Ocean	371.0	-17.6	-
Biosphere	8.34	21.5	3.26

Table 5.4. Exchange times calculated from Model 2

Reservoirs in exchange	Exchange time (τ, year)
Stratosphere - Troposphere	4.0
Troposphere - Surface Ocean	9.3
Surface - Deep Ocean	11.1
Troposphere - Biosphere	6.8
Deep - Surface Ocean	505

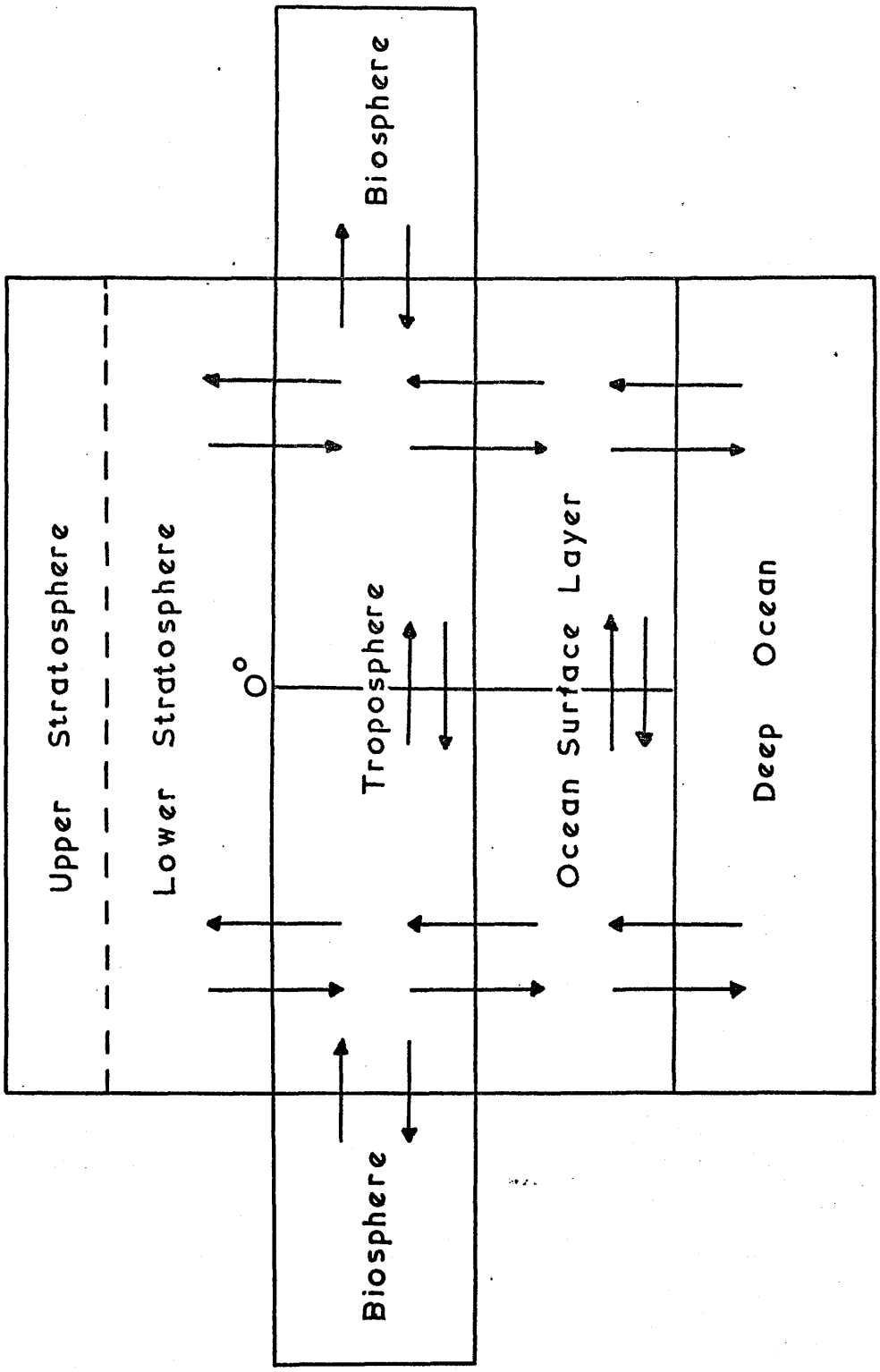


Figure 5.5. Model 3.

oceans and the troposphere is related only to the surface area of oceans exposed to the atmosphere. It is believed that this assumption will not incur a large error because the flux of CO_2 into the ocean per cm^2 must be about the same over the surface of the ocean. This is so because the flux of CO_2 into the ocean is simply proportional to the number of molecules striking the surface, and thus depends only on partial pressure and temperature. Some deviation should occur because of partial pressure difference over the ocean surface, effects of roughness of the ocean on surface area, and temperature differences, but these effects are probably small. Thus the exchange times in the two hemispheres will be related to the areas of the oceans in the respective regions. A similar consideration was applied to the exchange between the surface and deep oceans.

The values of the parameters used for this model and the results of exchange times are shown in Table 5.5 and Table 5.6 respectively.

5.3.4. Model 4 (cyclic model)

In this cyclic equilibrium model the oceans have been subdivided into four boxes, the surface layer, the deep ocean, the Antarctic and the Arctic (Figure 5.6). The surface layer was assumed to cover the oceans in a belt between latitudes $55^{\circ}N$ and $50^{\circ}S$. This amounts to 81 percent of the area of the ocean being

Table 5.5. Parameters applied in Model 3

Reservoir	Reservoir size (R) x 10^{17} g carbon	Excess ^{14}C (x) %	Gradient (dx/dt) % per year
Stratosphere	1.05	157.6	-25.7
Northern Troposphere	2.76	56.68	-5.76
Southern Troposphere	2.76	53.07	-3.60
Northern Surface Ocean	3.50	12.9	0.7
Southern Surface Ocean	4.66	8.9	0.7
Deep Ocean	371.0	-17.6	-
Northern Biosphere	4.90	24.0	3.18
Southern Biosphere	3.44	18.0	3.14

Table 5.6. Exchange times calculated from Model 3

Reservoirs in exchange	Exchange time (τ, year)
Stratosphere – Troposphere (N)	8.0
Stratosphere – Troposphere (S)	8.0
Troposphere (N) – Troposphere (S)	4.4
Troposphere (N) – Surface Ocean (N)	10.7
Troposphere (S) – Surface Ocean (S)	8.0
Troposphere (N) – Biosphere (N)	5.8
Troposphere (S) – Biosphere (S)	8.9
Surface Ocean (N) – Surface Ocean (S)	20.9
Surface Ocean (S) – Surface Ocean (N)	27.8
Surface Ocean (N) – Deep Ocean	13.1
Surface Ocean (S) – Deep Ocean	9.8
Deep Ocean – Surface Ocean (N)	1390
Deep Ocean – Surface Ocean (S)	783

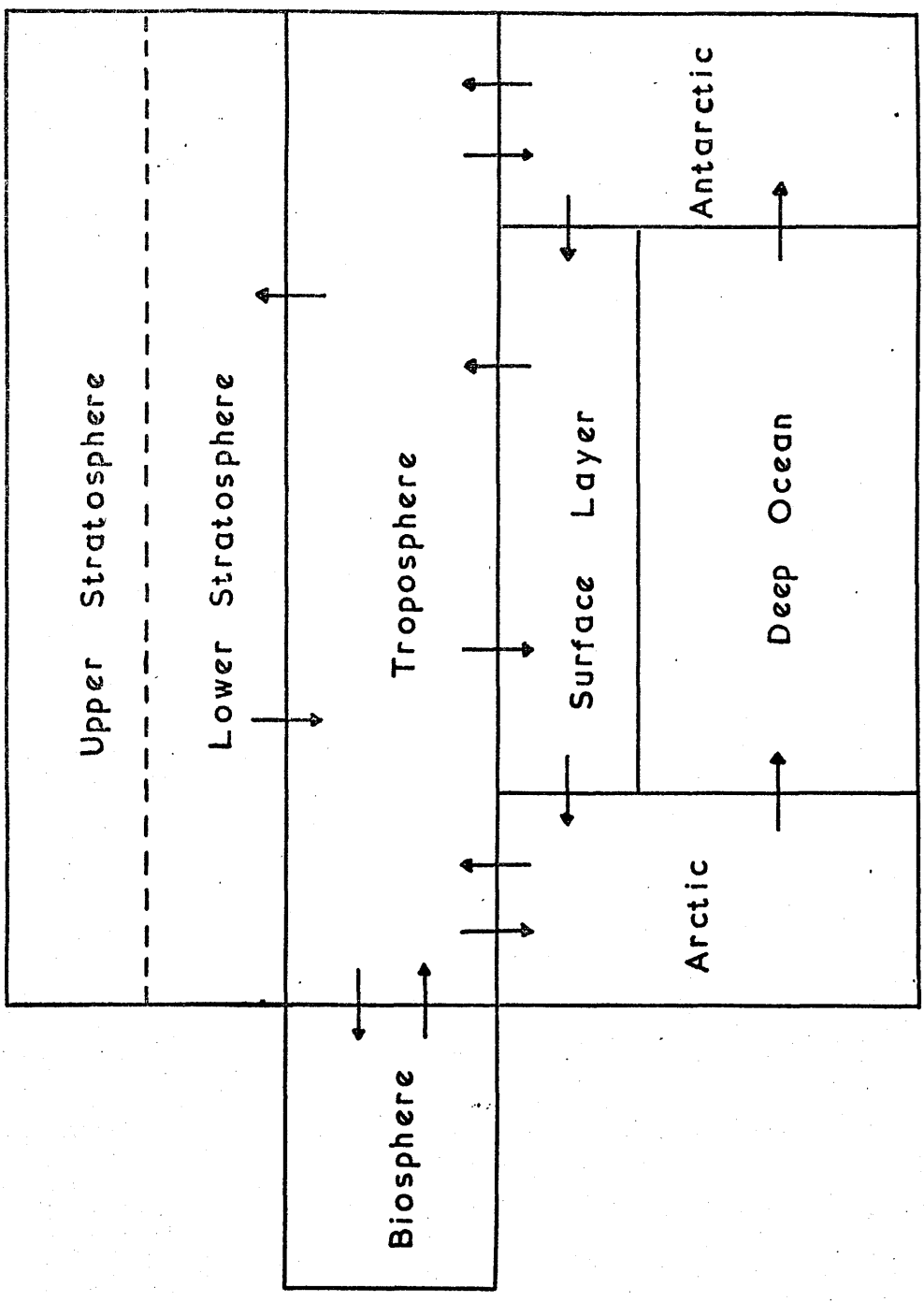


Figure 5.6. Model 4.

covered by the surface layer. The thermocline in this model is taken at 100 metres and assumed to be a major barrier to mixing between the two reservoirs with no transfer across it. Further, it was assumed that the water moves in the direction south to north in the surface and from north to south through the deep ocean, in accordance with oceanographic ideas. The excess carbon-14 concentration and gradient in the Arctic region was taken the same as in the surface layer and in the Antarctic region they were taken as the weighted means of the data of the surface layer and the deep ocean.

The values of parameters applied and the results are given in Table 5.7 and Table 5.8 respectively.

Attempts were made to construct more complex models for comparison but, as each additional reservoir adds the necessity for further assumptions and parameters, the available data did not allow much more complexity than that in the present models.

5.4. Discussion of the Results

Although the rate of transfer of carbon-14 across the tropopause shows seasonal dependence, a mean residence time of 4 years in the total stratosphere has been calculated, which is in reasonable agreement with the values determined by Hagemann et al (1959) and Nydal (1967). This value corresponds to an exchange rate of 4.3 moles $CO_2/m^2/y$ across the tropopause. It was also found that the exchange time for carbon-14 of about 2 years in the lower stratosphere before transfer to the tropo-

Table 5.7. Parameters applied in Model 4

Reservoir	Reservoir size (R) x 10^{17} g carbon	Excess ^{14}C (x) %	Gradient (dx/dt) % per year
Stratosphere	1.05	157.6	-25.7
Troposphere	5.52	54.9	-4.80
Biosphere	8.34	21.5	3.26
Surface Ocean	8.16	10.6	0.7
Arctic	4.80	10.6	0.7
Antarctic	50.4	-16.9	0.018
Deep Ocean	315.8	-17.6	-

Table 5.8. Exchange times calculated from Model 4

Reservoirs in exchange	Exchange time (τ, year)
Stratosphere - Troposphere	4.0
Troposphere - Biosphere	6.8
Troposphere - Surface Ocean	11.3
Troposphere - Arctic	72.8
Troposphere - Antarctic	302.1
Deep Ocean - Antarctic	546
Antarctic - Surface Ocean	87.2
Surface Ocean - Arctic	14.1
Arctic - Deep Ocean	8.3

sphere was very similar to the results derived from studies of stratospheric debris. Telegadas and List (1969) have recently studied the behaviour of particulate Sr-90 and gaseous carbon-14 in the stratosphere, and have shown that the average settling speed of Sr-90 was negligible after the first year of input. However, some disagreement exists between residence times calculated from carbon-14 and Sr-90. This they explain in terms of the input of carbon-14 at higher altitudes during the major test series of 1961-1962, and the finite vertical diffusion times within the stratosphere.

Although no interhemispheric stratospheric mixing times could be calculated directly from the observed and extrapolated data in both the upper and lower stratospheres for 1967 and 1968 it can be inferred that horizontal exchange times are probably less than 2 years. Such a period would permit horizontal homogeneity to occur between 1962, the end of the last major test series, and early 1967 when homogeneity appears to have been attained. On the other hand, there is no doubt that vertical inhomogeneities exist throughout the stratosphere with respect to carbon-14 concentrations, even in 1968. This observation, therefore, is a limiting feature in box model treatments which assume homogeneity throughout the particular boxes chosen.

The value of 9.3 years for the exchange time (which corresponds to an exchange rate of 13.7 moles $CO_2/m^2/y$) between the troposphere and surface ocean calculated from the first two

models is in agreement with the previously estimated values, using different approaches, i.e., from consideration of the known annual production of carbon-14 by cosmic rays and the steady state carbon-14 distribution in the various exchangeable reservoirs of carbon, Craig (1957) has calculated the exchange time between atmosphere and ocean to be 7 ± 3 years. As mentioned above, Revelle and Suess (1957) estimated the atmospheric exchange time to be 10 years from the magnitude of the industrial effect and steady-state carbon-14 distribution in the atmosphere and ocean. Using an approach similar to that presented here Nydal (1968) has estimated that the exchange time must lie between 5 and 10 years.

The shorter exchange time (8.0y) of carbon dioxide between southern hemisphere troposphere and surface ocean than between northern hemisphere troposphere and surface ocean (10.7y), as calculated from the model 3, is expected because of the larger surface area of the ocean in the southern hemisphere.

It is difficult to assign a value for the residence time of carbon-14 in the biosphere due to the inhomogeneous nature of this reservoir. Carbon-14 has different exchange times in different components of the biosphere. However, using the assumption that this box mised rapidly 6.8 years was found for the exchange time between the troposphere and biosphere. Since this is obviously not a true representation of the real system the value is liable to be smaller than the true value.

It is interesting that the exchange times between the troposphere and ocean, and the troposphere and biosphere reservoirs are comparable, i.e., the fluxes of CO_2 across the respective boundaries are similar. In considerations of the maintenance of steady-state carbon distribution the oceanic reservoir must still be the dominant contributor because of its relatively large mass. In comparison, the biosphere can be regarded as a smaller sink (sink size is proportional to R). Therefore any atmospheric deviation from the steady-state will be equally counteracted by the ocean and biosphere initially. However, since the overall buffering capacity is governed by the sink size the ocean will be effective long after the biospheric capacity has been exhausted, i.e., assuming constant reservoir size.

The interhemispheric tropospheric mixing time, 4.4 years, is probably subject to a large error due to the almost homogeneous nature of the troposphere during the period of measurement and the consequent difficulty in applying box model assumptions. This slow mixing rate should produce an appreciable difference in the observed Suess effects in the northern and the southern hemispheres due to much greater industrial activities in the northern hemisphere than southern hemisphere. According to Suess (1955) the industrial effect in the southern hemisphere may in fact be only half the same effect in the northern hemisphere, but a great many precise measurements will be needed to establish the exact

magnitude of this difference.

An exchange time of about 11 years between the surface ocean and deep ocean was calculated. There are few results published for comparison but the value of 11 years found here falls between the result (5-8 years) given by Broecker and Olson (1960) and (20-40 years) given by Craig (1958).

The exchange times calculated for the transfer of CO_2 from the deep ocean water to surface water are of most interest. The results of 505-550 years from the chain and cyclic models are somewhat lower than earlier estimates of Broecker and Olson (1960), Craig (1958), Rafter and Fergusson (1958). It is also interesting to note that in the ocean surface layer the exchange time between the hemispheres is about twice as large as the vertical exchange time.

The errors involved in the numerical values may be summarized as follows: At present the most uncertain values are probably the estimated sizes of the biosphere and the surface ocean reservoirs. The values appearing in the literature range from 8.34×10^{17} g carbon to 14.03×10^{17} g for the biosphere and from 7.65×10^{17} g to 8.16×10^{17} g for the surface ocean.

The excess carbon-14 concentrations and therefore the gradients used for the surface ocean and biosphere are also subject to considerable errors due to inconsistency in the available results. For example the calculated "standard deviation" was almost 40% of the average value in the surface ocean.

In calculations it was assumed that $^{12}CO_2$ and $^{14}CO_2$ rate constants are identical. In fact, the exchange rate constant for absorption of $^{12}CO_2$ into the ocean will be slightly greater than the rate constant for $^{14}CO_2$ because of an isotopic effect. Craig (1957) has estimated that the difference in exchange times of $^{12}CO_2$ and $^{14}CO_2$ between the atmosphere and ocean is about 3%. Finally, the magnitudes of the Suess effect in different reservoirs are not known accurately, however, the error on the exchange times introduced by this effect is believed to be not more than 5%.

A reasonable estimate of the maximum overall error possible in the exchange times is in the range of $\pm 50\%$.

5.5. Conclusions

The conclusions may be summarized as follows;

1) The stratospheric exchange times for CO_2 now seem well established. It is interesting to note the similarities between the results obtained from carbon-14 study and the behaviour of particulate products several years after weapons tests.

2) It is difficult to make more precise estimates of the time required for mixing processes within and between the troposphere and ocean since great uncertainties exist concerning (a) the size and turnover rate of the biosphere, and (b) the patterns and rates of mixing in the ocean. Precise estimates must await further work.

3) Regardless of the model selected steady-state assumptions require that on the average, carbon-14 remains in the deep oceans for at least 500 years.

4) The level of artificial carbon-14 in the atmosphere up to the present time has been controlled equally by the biosphere and ocean. The biospheric and atmospheric specific activities will reach equilibrium within the next decade and thereafter the atmospheric carbon-14 concentration will be controlled solely by the action of the oceanic reservoir, assuming that no further production of carbon-14 occurs as a result of weapons' testing.

APPENDIX A

Coputer Programme (ALGOL) for Determination of Best Straight Line Fit Through Observed Points.

```
begin  comment  This programme works out  and c for the
           equation y = mx + c by least squares from n
           pairs of x and y and gives the rs error
           (sqrt( [v↑2]/(n - 2) ) plus the individual
           deviations in y ;

integer  n, i, p;
real  sx, sy, sxy, sx2, sy2, m, c, d;
open(20);  open(70);
 start:  n:= read(20);
begin  array  x,y, e [1:n];
sx:=sy:=sxy:=sx2:=sy2:=0.0;
for i:=1 step 1 until n do
begin  x[i]:= read(20);
       y[i]:= read(20)
end;
for i:=1 step 1 until n do
begin sx:= sx + x[i];
      sy:= sy + y[i];
      sxy:=sxy + x[i]×y[i];
      sy2 := sy2 + y[i]↑2;
      sx2:=sx2 + x[i]↑2
end;

d:= n×sx2 -sx↑2;   m:= (n × sxy -sx × sy)/d;
c:= (sx2 × sy - sx × sxy)/d;
d:= sqrt((sy2 - sy × c - sxy × m)/(n - 2));

for i:= 1 step 1 until n do
 begin
 e[i] := y[i];
 y[i] := y[i] - m × x[i] - c
 end;
```

```
write text (70, [[4c] m*=*]);
write (70, format ([-d.ddddd10-nd]), m);
write text (70, [[3s]c*=*]);
write (70, forat([-d.ddddd10-nd]), c);
write text (70, [[3s] rms*error*=*]);
write (70, forat ([-d.ddddd10-nd]), d);
write text (70, [[3c][6s]y*obs[8s]y*calc [7s]deviation[2c]]);
 for i := 1 step 1 until n do
  begin
    write (70, format ([2s -d.dddd10-nd]), e[i]);
    write (70, format ([3s -d.dddd10-nd]), m × x[i] + c);
    write (70, format ([3s -d.dddd10-ndc]), y[i])
end;
comment  if another set of data is to follow punch 1 otherwise 0;

p := read (20);
if p = 1 then goto start;
close (70);
close (20);
comment The data tape consists of n followed by n pairs of
    values of x and y.  A 1 is punched after each set of n
    pairs if another set follows, and a zero after the
    final set;

end   end  →
```

APPENDIX B

Computer Programme (ALGOL) for Determination of Best Periodical Curve Fit Through Observed Points.

```
begin comment This programme estimates by the method of least
                squares the best values for A,B,C,b and c for
                a fixedvalue of t in the expression
                y=A+Bexp(-bt)+Cexp(-ct)Sin(2π(t-t0)) within a
                given range of b and c valuesto fit n
                observed points;
integer n,i,j,k,f1,f2,f3,f4;realsum1,sum2,sum3,sum4,sum5,sum6,
sum7,sum8,sum9,sum10,sum11,sum12,sum13,sum14,a,b,c,a1,a2,b1,b2,
d1,d2,c1,c2,s;
open(20);open(70);k:=read(20);
forj:=1step1until1kdo
begin n:=read(20);
begin real arrayx,y,e1,e2[1:n];
b1:=read(20);
b2:=read(20);
d1:=read(20);
d2:=read(20);
c1:=read(20);
c2:=read(20);
fori:=1step1until1ndo
beginx[i]:=read(20);
y[i]:=read(20)
end;
for a1:=b1stepd1until1c1do
for a2:=b2stepd2until1c2do
beginsum1:=sum2:=sum3:=sum4:=sum5:=sum6:=sum7:=sum8
          :=sum9:=sum10:=0;
fori:=1step1until1ndo
beginsum1:=sum1+1;
sum2:=sum2+exp(-a1xx[i]);
sum3:=sum3+exp(-a2xx[i])xsin(2x3.1416x(x[i]-t));
sum4:=sum4+y[i];
sum5:=sum5+exp(-2xa1xx[i]);
sum6:=sum6+exp(-(a1+a2)xx[i])xsin(2x3.1416x(x[i]-t));
sum7:=sum7+y[i]xexp(-a1xx[i]);
sum8:=sum6;
```

```
sum9:=sum9+exp(-2xa2xx[i])x(sin(2x3.1416x(x[i]-t)))↑2;
sum10:=sum10+y[i]xexp(-a2xx[i])xsin(2x3.1416x(x[i]-t));
end;
sum11:=sum1xsum5xsum9+sum2xsum8xsum3+sum2xsum6xsum3
        -sum5xsum3↑2-sum1xsum6xsum8-sum9xsum2↑2;
sum12:=sum4xsum5xsun9+sum7xsum8xsum3+sum2xsum6xsum10
        -sum3xsum5xsum10-sum2xsum7xsum9-sum4xsum8xsun6;
sum13:=sum1xsum7xsum9+sum2xsum10xsum3+sum4xsum6xsum3
        -sum7xsum3↑2-sum1xsum6xsum10-sum2xsum4xsum9;
sum14:=sum1xsum5xsum10+sum2xsum8xsum4+sum2xsum7xsum3
        -sum3xsum4xsum5-sum1xsum7xsum8-sum10xsum2↑2;
a:=sum12/sum11;
b:=sum13/sum11;
c:=sum14/sum11;
s:=0.0;
fori:=1step1until1ndo
begine1[i]:=a+bxexp(-a1xx[i])+cxexp(-a2xx[i])
                xsin(2x3.1416x(x[i]-t));
e2[i]:=e1[i]-y[i];
s:=s+e2[i]xe2[i]
end;
f1:=format([7s-d.ddd10+nd]);
f2:=format([7s-d.ddd10+nd]);
f3:=format([11s-d.ddd10+nd]);
f4:=format([10s-d.ddd10+ndc]);
write(70,f1,a1);
write(70,f2,a2);
write(70,f3,s);
write(70,f1,a);
write(70,f1,b);
write(70,f4,c)
end;
end;
end;
close(20);close(70);
comment The data tape consists of the number of separate sets
 of data,k,then the number of pairs of points,n,follwed by
 the lower limits of b and c, then the increments in b and c
 desired, then theupper limits of b and c, and finally the
 coordinates of the n points (y,t). The output lists values
 of s, which is related to the deviation between observed
 and calculated points, so that the best values of A,B,C,
 b and c correspond to the minimum value of s;

end→
```

APPENDIX C

Computer Programme (ALGOL) for Determination of Best Exponential Fit Through Observed Points.

```
begin comment This programme estimates by the method of least
                squares the best values for A, and k in the
                expression y=Aexp(-kt) within a given  range
                of k valuesto fit n observed points;
integer k,j,i,n,f1,f4; real sum1,sum2,a,a1,b1,d1,c1,s;
open(20); open(70); k:=read(20);
for j:=1 step 1 until k do
begin n:=read(20);
begin real array x,y,e1,e2[1:n];
b1:=read(20);
d1:=read(20);
c1:=read(20);
for i:=1 step 1 until n do
begin x[i]:=read(20);
      y[i]:=read(20)
end;
for a1:=b1 step d1 until c1 do
begin sum1:=sum2:=0;
for i:=1 step 1 until n do
begin sum1:=sum1+exp(-2×a1××x[i]);
      sum2:=sum2+y[i]×exp(-a1××x[i])
end;
a:=sum2/sum1;
    s:=0.0;
for i:=1 step 1 until n do
begin e1[i]:=a×exp(-a1××x[i]);
       e2[i]:=e1[i]-y[i];
      s:=e2[i]×e2[i]
end;
f1:=format([7s-d.ddd10+nd]);
f4:=format([10s-d.ddd10+ndc]);
write(70,f1,a1);
write(70,f1,s);
```

```
write(70,f4,a)
end;
end;
end;
close(20); close(70);
comment The data tape consists of the number of separate
 sets of data, then the number of pairs of points,n,
 follwed by the lower limit of k, then the increment
 in k desired, then the upper limit of k, and finally
 the coordinates of the n points (y,t). The output
 lists values of s, which is related to the deviation
 between observed and calculated points, so that the
 best value of A and k correspond to the minimum
 value of s;
end→
```

REFERENCES

Anderson, E.C. (1953). The production and distribution of natural radiocarbon. Ann. Rev. Nuclear Sci., 2, 63-78.

Anderson, E.C. and Libby, W.F. (1951). World-wide distribution of natural radiocarbon. Phys. Rev., 81, 64-69.

Anderson, E.C., Libby, W.F., Weinhouse, S., Reid, A.F., Kirshenbaum A.D. and Grosse, A.V. (1947). Radiocarbon from cosmic radiation. Science, 105, 576-577.

Arnold, J.R. and Anderson, E.C. (1957). The distribution of carbon-14 in nature. Tellus, 1, 9, 28-32.

Barendsen, G.W. (1957). Radiocarbon dating with liquid CO_2 as diluent in a scintillation solution. Rev. Sci. Instrum., 28, 430-432.

Barker, H. (1958). Radiocarbon dating: Its scope and limitations. Antiquity, 32, 253-263.

Baxter, M.S. (1969). Recent fluctuations of atmospheric carbon-14 concentrations. Ph.D.thesis, University of Glasgow.

Bien, G.S., Rakestraw, N.W. and Suess, H.E. (1963). Radiocarbon dating of deep water of the Pacific and Indian Oceans. Radioactive Dating, IAEA, Vienna, 159-173.

Bien, G.S. and Suess, H.E. (1967). Transfer and exchange of ^{14}C between the atmosphere and the surface water of the Pacific Ocean. Radioactive Dating and Methods of Low-Level Counting, IAEA, Vienna, 105-115.

Bischof, W. and Bolin, B. (1966). Space and time variations of the CO_2 content of the troposphere and lower stratosphere. Tellus, 18, 155-159.

Bolin, B. and Keeling, C.D. (1963). Large-scale atmospheric mixing as deduced from the seasonal and meridional variations of carbon dioxide. J. Geophys. Res., 68, 3899-3920.

Bray, J.R. (1965). Atmospheric carbon-14 content during the past three millennia in relation to temperature and solar activity. Nature, 209, 1065-1067.

Broecker, W.S., Gerard, R., Ewing, M. and Heezen, B.C. (1960). Natural radiocarbon in the Atlantic Ocean. J. Geophys. Res., 65, 2903-2931.

Broecker, W.S. and Olson, E.A. (1960). Radiocarbon from nuclear tests, II. Science, 132, 718-721.

Broecker, W.S. and Olson, E.A. (1961). Lamont radiocarbon measurements, 8. Radiocarbon, 3, 176-204.

Broecker, W.S. and Walton, A. (1959). Radiocarbon from nuclear tests. Science, 130, 309-314.

Burke, W.H. and Meinschein, W.G. (1954). Methane proportional counter method for ^{14}C age determinations. Phys. Rev., 93, 915.

Burke, W.H. and Meinschein, W.G. (1955). ^{14}C dating with a methane proportional counter. Rev. Sci. Instrum., 26, 1137-1140.

Callow, W.J., Baker, M.J. and Hassell, C.I. (1965). National Physical Laboratory radiocarbon measurements, III. Radiocarbon and Tritium Dating, Pullman, Washington, Conf-650652, 393-395.

Cambray, R.S., Fisher, E.M.R., Brooks, W.L. and Peirson, D.H. (1968). Radioactive fallout in air and rain results to the middle of 1968. AERE - R 5899.

Craig, H. (1953). The geochemistry of the stable carbon isotopes. Geochim. et cosmoch. Acta, 3, 53-92.

Craig, H. (1957). The natural distribution of radiocarbon and the exchange time of carbon dioxide between atmosphere and sea. Tellus, 9, 1-17.

Craig, H. (1958). Distribution of radiocarbon and tritium, and the

production rate of natural tritium. Nat. Acad. Sci., NRC publication No. 572, 135-155.

Craig, H. (1961). Mass-spectrometer analyses of radiocarbon standards. Radiocarbon, 3, 1-3.

Craig, R. (1965). The Upper Atmosphere. New York, Academic Press.

Crane, H.R. (1954). Andover Conf. on Radiocarbon Dating, Phillips Academy, October 21-23.

Damon, P.E. (1965). Radiocarbon and climate. INQUA Congr. 7th Boulder and Denver, Colo., presented paper.

Damon, P.E., Long, A. and Grey, D.C. (1965). Fluctuation of atmospheric ^{14}C during the last six millennia. Radiocarbon and Tritium Dating, Pullman, Washington, Conf. - 650652, 415-428.

Damon, P.E., Long, A. and Grey, D.C. (1966). Fluctuations of atmospheric ^{14}C during the last six millennia. J. Geophys. Res., 71, 1055-1063.

Danielsen, E.F. (1965). Radioactivity and potential vorticity. Radioactive Fallout from Nuclear Weapons Tests, USAEC, Conf. - 765, 436-449.

DeVries, Hl. (1958). Variation in concentration of radiocarbon with time and location on earth. Koninkl. Ned. Akad. Wetensch., Proc., Ser., B61, 94-102.

DeVries, Hl. and Barendsen, G.W. (1952). A new technique for the measurement of age by radiocarbon. Physica, 18, 652.

DeVries, Hl. and Barendsen, G.W. (1953). Radiocarbon dating by a proportional counter filled with carbon dioxide. Physica, 19, 987-1003.

DeVries, Hl. and Barendsen, G.W. (1954). Measurements of age by the carbon-14 technique. Nature, 174, 1138-1141.

DeVries, Hl. (1955). Purification of CO_2 for use in a proportional counter for carbon-14 age measurements. Appl. Sci. Res., B, 5, 387-400.

Diethorn, W. (1956). A methane proportional counter system for natural radiocarbon measurements. Carnegie Inst. Technology, U.S. Atomic Energy Rept. NYO - 6628, 1, 146.

Dingle, A.N. (1954). The carbon dioxide exchange between the North Atlantic Ocean and the atmosphere. Tellus, 6, 342-350.

Dyck, W. (1965). Secular variations in the ^{14}C concentration of Douglas fir tree rings. Radiocarbon and Tritium Dating, Pullman, Washington, Conf. - 650652, 440-452.

Elsasser, W., Ney, E.P. and Winckler, J.R. (1956). Cosmic ray intensity and geomagnetism. Nature, 178, 1226-1227.

Eriksson, E. (1963). Possible fluctuations in atmospheric carbon dioxide due to changes in the properties of the sea. J. Geophys. Res., 68, 3871-3876.

Fairhall, A.W., Schell, W.R. and Takashima, Y. (1961). Apparatus for methane synthesis for radiocarbon dating. Rev. Sci. Instrum., 32, 323-325.

Faltings, V. (1952). The measurement of ^{14}C activity in the proportionality counter. (AERE - Trans - 11/3/5/283), translated from Naturwissenschaften, 39, 378-379.

Feely, W.H., Biscaye, P.E., Davidson, B. and Seitz, H. (1966). Project Stardust, eleventh prog. rept., DASA - 1821.

Ferguson, C.W. (1968). Bristlecone pine: Science and esthetics. Science, 159, 839-846.

Fergusson, G.J. (1955). Radiocarbon dating system. Nucleonics, 13 (1), 18-23.

Fergusson, G.J. (1957). Reduction of atmospheric radiocarbon concentration by fossil fuel carbon dioxide and the mean life of carbon dioxide in the atmosphere. Proc. Roy. Soc. London, A, 243, 561.

Godwin, H. (1962). Half-life of radiocarbon. Nature, 195, 984.

Goody, R.M. (1954). The Physics of the Stratosphere. London, Cambridge University Press.

Harkness, D.D. (1969). Private communication, University of Glasgow.

Hagemann, F.T., Gray, J. and Machta, L. (1965). Carbon-14 measurements in the atmosphere - 1963 to 1964. USA, HASL - 159.

Hagemann, F.T., Gray, J., Machta, L. and Turkevich, A. (1959). Stratospheric carbon-14, carbon dioxide and tritium. Science, 130, 542-552.

Harley, N., Fisenne, I., Ong, L.D.Y. and Harley, J. (1965). Fission yield and fission product decay. HASL - 164, 255.

Hayes, F.N., Anderson, E.C. and Arnold, J.R. (1955). Liquid scintillation counting of natural radiocarbon. Proc. of the Intern. Conf. on the Peaceful Uses of Atomic Energy, U.N., 14, 188-192.

Houtermans, J. (1966). On the quantitative relationship between geophysical parameters and the natural ^{14}C inventory. Z. Physik., 193, 1-12.

Houtermans, J. and Suess, H.E. (1967). Effect of industrial fuel combustion on the carbon-14 level of atmospheric CO_2. Radioactive Dating and Methods of Low-Level Counting, IAEA, Vienna, 57-68.

Hughes, E.E. and Mann, W.B. (1963). The half-life of carbon-14: Comments on the mass-spectrometric method. Intern. J. Appl. Radiation Isotopes, 15, 97-100.

Junge, C.A. (1961). Note on the exchange rate between the northern and southern atmosphere. Tellus, 14, 242.

Junge, C.E. and Czeplak, G. (1967). Some aspects of the seasonal variation of carbon dioxide and ozone. Tellus, 20, 422-434.

Kanwisher, J. (1963). Effect of wind on CO_2 exchange across the sea surface. J. Geophys. Res., 68, 3921-3927.

Kigoshi, K. (1965). Secular variation of atmospheric radiocarbon concentration and its dependence on geomagnetism. Radiocarbon and Tritium Dating, Pullman, Washington, Conf. - 650652, 429-438.

Kigoshi, K. and Hasegawa, H. (1966). Secular variations of atmospheric radiocarbon and its dependence on geomagnetism. J. Geophys. Res., 71, 1065-1071.

Korff, S.A. (1940). Terrestrial magnetism and atmospheric electricity. 45, 133.

Kouts, H.J. and Yuan, L.C.L. (1952). The production rate of cosmic-ray neutrons and ^{14}C. Phys. Rev., 86, 128-129.

Kusumgar, S. (1963). Radiocarbon dating techniques. Proc. Ind. Acad. Sci., 58, 125-140.

Ladenburg, R. (1952). The absorption rate of cosmic-ray neutrons producing ^{14}C in the atmosphere. Phys. Rev., 86, 128-129.

Lal, D. and Rama (1965). Atmospheric pathways of man-made C^{14}, H^3 and Sr^{90}. Radiocarbon and Tritium Dating, Pullman, Washington, Conf. - 650652, 541-545.

Lal, D. and Rama (1966). Characteristics of global tropospheric mixing based on man-made C^{14}, H^3 and Sr^{90}. J. Geophys. Res., 71, 2865-2874.

Leipunsky, O.I. (1957). The radiation hazards of ordinary explosions of pure hydrogen and ordinary atomic bombs. Atomnaya Energiia, 3, 530-539.

Leith, H. (1963). The role of vegetation in the carbon dioxide content of the atmosphere. J. Geophys. Res., 68, 3887-3898.

Libby, W.F. (1955). Radiocarbon Dating. Univ. of Chicago Press., 2nd ed.

Libby, W.F. (1956). Radioactive fallout and radioactive strontium. Science, 123, 657-658.

Libby, W.F. (1959). Radioactive fallout particularly from the Russian October series. Proc. Nat. Acad. Sci., 45, 959-976.

Libby, W.F. (1963). Accuracy of radiocarbon dates. Science, 140, 278-280.

Libby, W.F. (1965). Radiocarbon and paleomagnetism. Radiocarbon and Tritium Dating, Pullman, Washington, Conf. - 650652, 348-356.

Libby, W.F. and Arnold, J.R. (1946). Radiocarbon from pile graphite; chemical methods for its concentration. Argon National Lab., Lemont, III.

Lingelfelter, R.E. (1963). Production of carbon-14 by cosmic-ray neutrons. Rev. Geophys., 1, 35-55.

Long, A. (1965). Techniques of methane production for ^{14}C dating. Radiocarbon and Tritium Dating, Pullman, Washington, Conf. - 650652, 37-40.

Machta, L. (1959). Production of carbon-14 in nuclear explosions. Hearings of the joint committee on atomic energy, Congress of the United States, 3, 2191.

Mann, W.B., Marlow, W.F. and Hughes, E.E. (1961). The half-life of carbon-14. Intern. J. Appl. Radiation Isotopes, 11, 57-67.

Moscicki, W. (1958). The use of G.M. counters filled with a mixture of CO_2 and CS_2 for the measurement of the activity of natural carbon. Part II. Experiments with G.M. counters filled with CO_2 + CS_2 used for detection of ^{14}C in natural carbon. Acta. Phys. Polon, 17, 327-343.

Münnich, K.O. and Roether, W. (1967). Transfer of bomb ^{14}C and tritium from the atmosphere to the ocean. Internal mixing of the ocean on the basis of tritium and ^{14}C profiles. Radioactive Dating and Methods of Low-Level Counting, IAEA, Vienna, 93-104.

Münnich, K.O. and Vogel, J.C. (1963). Investigation of meridional transport in the troposphere by means of carbon-14 measurements. Radioactive Dating, IAEA, Vienna, 189-197.

Nydal, R. (1963). Increase in radiocarbon from the most recent series of thermonuclear tests. Nature, 200, 212-214.

Nydal, R. (1967). On the transfer of radiocarbon in nature. Radioactive Dating and Methods of Low-Level Counting, IAEA, Vienna, 119-128.

Nydal, R. (1968). Further investigation on the transfer of radiocarbon in nature. J. Geophys. Res., 73, 3617-3635.

Nydal, R. (1969). Private communication, Trondheim, Norway.

Nydal, R. and Lövseth, K. (1965). Distribution of radiocarbon from nuclear tests. Nature, 206, 1029-1031.

Olson, E.A. and Nickoloff, N. (1965). A system for methane synthesis. Radiocarbon and Tritium Dating, Pullman, Washington, Conf. - 650652, 41-52.

Olsson, I.U. (1958). A ^{14}C dating station using the CO_2 proportional counting method. Ark. Fys., 13, 37-60.

Olsson, I.U. (1968). Modern aspects of radiocarbon datings. Earth-Sci. Rev., 4, 203-218.

Olsson, I.U. and Karlén, I. (1963). The half-life of ^{14}C and the problems which are encountered in absolute measurements on beta-decaying gases. Radioactive Dating, IAEA, Vienna, 1-11.

Olsson, I.U. and Stenberg, A. (1967). Very high ^{14}C activity in the Abisko, Sweden, during summer, 1965. Radioactive Dating and Methods of Low-Level Counting, IAEA., Vienna, 69-78.

Olsson, I.U., Karlén, I., Turnbull, A.H. and Prosser, N.J.D. (1962). A determination of the half-life of ^{14}C with a proportional counter. Arkiv. Fysik, 22, 237-255.

Palmer, B.D. (1969). Interhemispheric transport of atmospheric fission debris from French nuclear tests. Science, 164, 951-952.

Plass, G.N. (1956). The carbon dioxide theory of climatic change. Tellus, 8, 140-154.

Rafter, T.A. (1965). Carbon-14 variations in nature. Part 2 - Increase in ^{14}C activity in the atmosphere of the southern hemisphere from the testing of nuclear weapons. New Zealand J. Sci., 8, 472-493.

Rafter, T.A. (1968). Carbon-14 variations in nature. Part 3 - ^{14}C measurements in the south Pacific and Antarctic Oceans. New Zealand J. Sci., 11, 551-589.

Rafter, T.A. and Fergusson, G.J. (1957). Atom bomb effect - Recent increase of carbon-14 content of the atmosphere and biosphere. Science, 126, 557-558.

Rafter, T.A. and Fergusson, G.J. (1958). Atmospheric radiocarbon as a tracer in geophysical circulation problems. Proc. 2nd Intern. Conf. Peaceful Uses of Atomic Energy, 18, 526-532.

Revelle, R. and Suess, H.E. (1957). Carbon dioxide exchange between atmosphere and ocean and the question of an increase of atmospheric CO_2 during the past decades. Tellus, 9, 18-27.

Sharp, A.R. and Ellis, J.G. (1965). System design in low background internal gas sample counting of carbon-14 and tritium.

Radiocarbon and Tritium Dating, Pullman, Washington, Conf. - 650652, 17-28.

Soberman, R.K. (1956). High altitude cosmic-ray neutron intensity variations. Phys. Rev., 102, 1399-1409.

Stuiver, M. (1961). Variations in radiocarbon concentration and sunspot activity. J. Geophys. Res., 66, 273-276.

Stuiver, M. (1965). Carbon-14 content of 18th and 19th century wood: Variation correlated with sunspot activity. Science, 149, 533-534.

Stuiver, M. (1965). Variations in radiocarbon concentration in tree rings in north America during the 18th and 19th centuries. Radiocarbon and Tritium Dating, Pullman, Washington, Conf. - 650652, 452.

Stuiver, M. (1967). Origin and extent of atmospheric ^{14}C variations during the past 10,000 years. Radioactive Dating and Methods of Low-Level Counting, IAEA, Vienna, 27-40.

Stuiver, M. and Suess, H.E. (1966). On the relationship between radiocarbon date and true sample ages. Radiocarbon, 8, 534-539.

Suess, H.E. (1953). Natural radiocarbon and the exchange of carbon dioxide between the atmosphere and the sea. Nuclear Processes in Geologic Settings, NRC publ., 52-56.

Suess, H.E. (1954). Natural radiocarbon measurements by acetylene counting. Science, 120, 5-7.

Suess, H.E. (1955). Radiocarbon concentration in modern wood. Science, 122, 415-417.

Suess, H.E. (1965). Secular variations of the cosmic-ray produced carbon-14 in the atmosphere and their interpretations. J. Geophys. Res., 70, 5937-5952.

Suess, H.E. (1965). Secular changes of natural radiocarbon and their interpretation. Radiocarbon and Tritium Dating, Pullman, Washington, Conf. - 650652, 439.

Takahashi, T. (1961). Carbon dioxide in the atmosphere and in the Atlantic Ocean water. J. Geophys. Res., 66, 477-494.

Takahashi, T. (1967). Carbon dioxide cycle in the sea and atmosphere. The Encyclopedia of Atm. Sci. and Astrogeology, 131-135.

Tauber, H. (1961). Latitudinal effect in the transfer of radiocarbon from stratosphere to troposphere. Science, 133, 461-462.

Telegadas, K. and List, R.J. (1969). Are particulate radioactive tracers indicative of stratospheric motions? J. Geophys. Res., 74, 1339-1350.

Walker, S.A.S. (1969). Carbon-14 concentration variations in ground level air. B.Sc. Thesis, University of Glasgow.

Walton, A., Feely, H.W., Tucek, C.S. and Kologrivov, R. (1964). Stratospheric and tropospheric observations of radiocarbon from nuclear tests. Unpublished.

Walton, A., Baxter, M.S., Callow, W.J. and Baker, M.J. (1967). Carbon-14 concentrations in environmental materials and their temporal fluctuations. Radioactive Dating and Methods of Low-Level Counting, IAEA, Vienna, 41-47.

Willis, E.H., Tauber, H. and Münnich, K.O. (1960). Variations in the atmospheric radiocarbon concentration over the past 1300 years. Am. J. Sci., Radiocarbon Suppl., 2, 1-4.

Wood, L. and Libby, W.F. (1964). Geophysical implications of radiocarbon date descripencies. Isotopic and Cosmic Chemistry, Holland, Amsterdam, 205-210.

Young, J.A. and Fairhall, A.W. (1968). Radiocarbon from nuclear weapons tests. J. Geophys. Res., 73, 1185-1200.

ACKNOWLEDGEMENTS

I would like to express my gratitude to Dr. Alan Walton for his assistance, constructive criticism and encouragement throughout the course of this work.

I extend thanks to Messrs. Douglas D. Harkness and Murdoch S. Baxter for many helpful discussions and comments on this work.

The co-operation of the National Physical Laboratory in providing facilities for $^{13}C/^{12}C$ measurements is gratefully acknowledged.

I express my thanks to all the individuals and organisations, too numerous to detail, who collected the samples.

Thanks are due to Mrs. Margaret Currie for her careful reproduction of the figures used in this thesis.

Finally, I gratefully acknowledge the financial support of the Natural Environment Research Council, which made this work possible.